Study Protocol 172: Surface Water Monitoring for Forest Herbicides in the Yurok Tribal Territory

Pam Wofford

April 1999

STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
Environmental Hazards Assessment Program
830 K Street
Sacramento, California 95814-3510

Study 172

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California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management
830 K Street
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Study 172: Surface Water Monitoring for Forest Herbicides in the Yurok Aboriginal Territory

APPROVALS

Yurok Tribe of California — 9-11-99 — Date

Annie Yates
Sponsor (U.S. EPA) — 9/23/99 — Date

Ron Oshima FOR CDFA
Management (Dept. Pesticide Regulation) — 9-2-98 — Date

Pamela Wofford
Study Director (Dept. Pesticide Regulation) — 9/16/98 — Date

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Document Title: Study 172: Surface Water Monitoring for Forest Herbicides in the Yurok Aboriginal Territory

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Kean S. Goh
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APPROVED: Doug Okumura Date: 9-24-98
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Department of Pesticide Regulation
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April 1999

I. INTRODUCTION

Since time immemorial, the Yurok people occupied the Yurok ancestral territory, which encompasses the lower 52 miles of the Klamath River, from a short distance above the confluence of the Trinity to the sea, and a longer stretch of seacoast, from Damnation Creek, Del Norte County, to the Little River, in Humboldt County (Yurok Tribe, 1999). The Yurok Tribal Reservation boundary, partially designated in 1856 and reaffirmed in 1892, is located one mile each side of the lower Klamath River from Weitchpec to the mouth at Requa (Yurok Tribe, 1999). The reservation has a checkerboard pattern of Tribal, public, and privately owned property of which approximately 85 percent is privately owned. The majority of these private lands are owned by several timber companies.

An integral part of forestry management includes the use of herbicides to control vegetative competition to new seedlings during reforestation programs and stand improvement. These herbicides are used on private forest land watersheds which lie within and adjacent to Yurok ancestral and reservation lands. Annual rainfall averages 20 to 100 inches per year (Barrett, 1995) and the surface water supply originates from a massive network of smaller watersheds linked by streams throughout the hydrologic basin (California Department of Forestry, 1979). Studies conducted in other forested areas of California have shown that herbicide residues may be transported off-site in rain and/or snowmelt runoff water (Carlson and Fiore, 1993). Consequently, residents in these rural forest communities, who rely on surface water as a drinking water source, have expressed concern about the potential presence of herbicide residues in water.

The tribal people live in close contact with the land through fishing, hunting and gathering of plants for food, basketry and medicinal uses. The tribal people of northwestern California have requested that the California Department of Pesticide Regulation (DPR) and the U.S. Environmental Protection Agency (EPA) Office of Pesticide Programs monitor surface waters for herbicides used in reforestation practices in that region. Herbicides to be monitored include atrazine, hexazinone,

2,4-dichlorophenoxyacetic acid (2,4-D), glyphosate, and triclopyr, all of which are compounds currently registered in California for forestry use.

II. OBJECTIVE

This project is a preliminary investigation to determine the presence of herbicide residues in surface waters of northwestern California. The North Coast Regional Water Quality Control Board's (Regional Water Board) Water Quality Control Plan for the North Coast Region operational standard of 10 ppb will be used as the basic criteria to measure compliance with the Best Management Plan for all of the herbicides monitored. The Regional Water Board will be notified of any concentrations which exceed the 10 ppb standard. If the results of this study indicate that herbicide residues are present in surface waters, then further investigation may be warranted to determine the extent of the problem and possible herbicide sources.

III. SPONSOR

Annie Yates
U.S. EPA, Region IX
Office of Pesticide Program
75 Hawthorne St.
San Francisco, California 94105-3905

IV. COLLABORATORS

Susan Burdick, Ken Childs, Sr., Troy Fletcher, Marilyn Hostler, Ron Johnson, Bessie Lee, Jene McCovey, Sef Murguia, Richard Myers, Robley Schwenk, Chuck Striplen (Hoopa Valley Tribal Council).

The Yurok Environmental Monitoring Work Group
The Yurok Tribe of California
1034 Sixth St.
Eureka, California 95501

V. TESTING FACILITIES AND PERSONNEL

The testing facilities are located at:

Department of Pesticide Regulation
Environmental Hazards Assessment Program
830 K Street
Sacramento, California 95814-3510

Department of Pesticide Regulation
Environmental Hazards Assessment Program
3971 Commerce Drive, Suite D
West Sacramento, California 95691

California Department of Food and Agriculture
Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, California 95832

This cooperative sampling effort will be conducted by DPR's Environmental Hazards Assessment Program (EHAP) staff, Yurok tribal representatives, U.S. EPA, and the County Agricultural Commissioners' staff, under the general direction of Kean S. Goh, Program Supervisor.

Key personnel are listed below:

Study Director:	Pam Wofford
Senior Staff Scientist:	Lisa Ross
Field Coordinator:	DeeAn Jones
Statistician:	Terri Barry
Quality Assurance/Lab Liaison:	Carissa Gana
Chemist:	Cathy Cooper
Contact Person:	Madeline Brattesani

Responsibilities of the key personnel are described in EHAP Standard Operating Procedure ADMN002.00 (Supplement 1). Authorship of the final report may include but not limited to Pam Wofford, DeeAn Jones, Kean Goh, Cathy Cooper, Terri Barry, and Lisa Ross.

Questions concerning this monitoring study should be directed to either 1) Madeline Brattesani at (916) 324-4100; fax, (916) 324-4088; e-mail, <mbrattesani@cdpr.ca.gov.> or 2) Kean Goh (same telephone and fax numbers as those given for Madeline Brattesani); e-mail, <kgoh@cdpr.ca.gov>.

VI. EXPERIMENTAL DESIGN/STUDY PLAN

A. Surface Water - General Investigation

A general investigation for herbicide residues in surface water will be conducted at up to five sites, which are to be selected by the Yurok Tribal representatives. During the Yurok Environmental Monitoring Workgroup meetings, the Yurok Tribal representatives had selected several creeks that were of interest. These included the Blue Creek, Hunter Creek, Pecwan Creek, Redwood Creek, Roach Creek and Wilson Creek (Figure 1). We

propose to sample water from any of the six creeks with current herbicide applications. Site selection will be based on proximity to herbicide applications, site accessibility, and importance to the local Indian Tribes. These sites will be sampled up to six times in the study year (1998-1999) during rain runoff and/or snowmelt events. The water samples will be analyzed for the herbicide(s) applied.

Water samples will be collected at the creek(s) during the first rain runoff event following the application, and in spring at the first sign of snowmelt runoff in the watershed of application area(s). One creek may be selected during runoff events for additional sampling over time. Samples will also be collected during periods of herbicide applications.

VII. SAMPLING METHODS, SAMPLE STORAGE, SAMPLE TRANSPORT, AND CHEMICAL ANALYTICAL METHODS

A. Water and Environmental Sampling Methods. Sample Storage, Transport, and Tracking Procedures.

When possible, water samples will be collected using a depth-integrated, equal width-increment method for sampling surface water (EHAP SOP FSWA003.00, Supplement 2). Under conditions of low flow or shallow depths, a grab sample will be taken. During rain runoff, an automatic pumping sampler with a fixed-depth intake may be used to assure prompt sample collection in remote areas. The automatic sampler allows for multiple discrete grab samples over time. Water samples will then be split into 1L amber glass bottles for each chemical analysis and preserved according to methods reported in EHAP Standard Operating Procedure FSWA004.00 (Supplement 3). Samples will be analyzed for the herbicides applied in the areas of the sampling site. Separate samples will be collected for a) glyphosate analysis, b) phenoxy analysis for 2,4-D and triclopyr, or c) triazine analysis for atrazine and hexazinone.

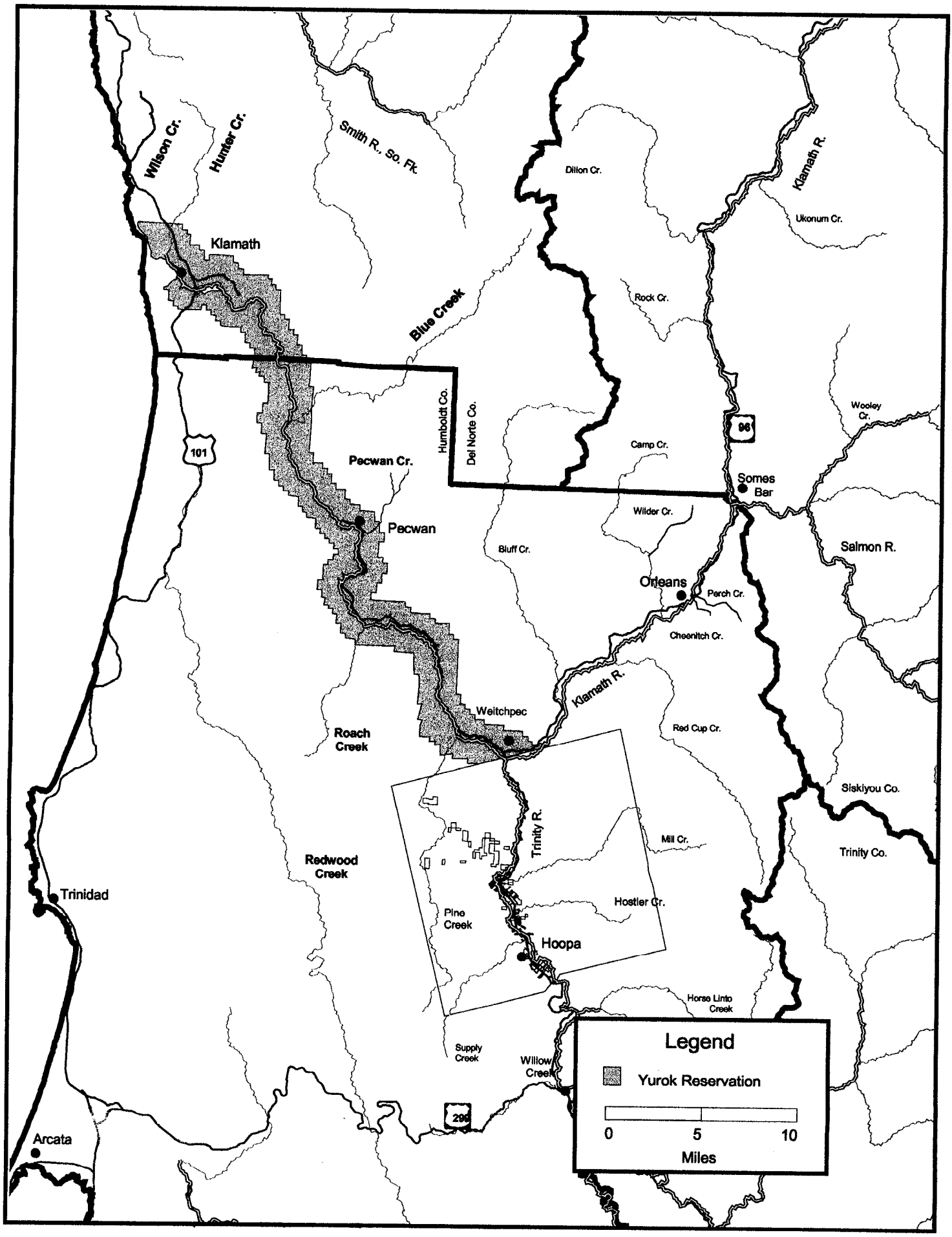
Additional duplicate water samples will be collected at each site during each sampling period and stored for possible later use (e.g., if sample breakage occurs with other collected samples). All water samples will be stored on wet ice and maintained at 4 °C as described in EHAP SOP QAQC004.00 (Supplement 4) until chemically extracted. Sample tracking is described in EHAP SOP QAQC003.00 (Supplement 5). Results will be reported in micrograms per liter (µg/L).

Environmental parameters such as air temperature, water temperature, pH, dissolved oxygen, and electrical conductivity will be recorded at each site for each sampling period.

B. Analytical Methods

Chemical analyses for herbicides in surface water will be performed by the California Department of Food and Agriculture Laboratory.

Figure 1. Yurok Reservation and Ancestral Region.



Method validation for the phenoxy, triazine, and glyphosate analysis to be used in surface water monitoring followed EHAP SOP QAQC001.00 (supplement 6). All method validation work has been completed for the five compounds. The spike levels were chosen based on the range of concentrations anticipated in surface water. The mean recovery and standard deviation were calculated for each compound. Warning limits were established at the mean recovery plus two times the standard deviation and the mean recovery minus two times the standard deviation. Control limits were established at the mean recovery plus three times the standard deviation and the mean recovery minus three times the standard deviation.

Method Detection Limits were determined according to EHAP SOP QAQC001.00 and the U.S. EPA procedure (40 CFR, Part 136, Appendix B). The Method Detection Limit for each chemical are given in the analytical method. The method validation work and analytical method for each chemical are located in supplement 7.

C. Quality Assurance/Quality Control

Laboratory continuing quality control will follow EHAP SOP QAQC001.00 and include the following: Matrix Blank: 1 matrix blank per extraction set and Matrix Spike: 2 matrix spike sample per extraction set. Any matrix spike samples falling outside the warning or control limits will have the appropriate corrective steps taken as described in EHAP SOP QAQC001.00. The spikes will be prepared by a chemist in another section of the analytical lab and submitted for analysis by the Quality Assurance/Lab Liaison.

For field QC, a set of equipment blank (one for each analysis) will be taken by each crew at least once during each collection period. These blanks will help determine if the sampling and splitting equipment was adequately cleaned. The collection of these blanks will follow EHAP SOP QAQC006.00 (Supplement 8).

Blind spike samples for QAQC will compromise approximately 10 percent of the total number of samples.

VIII. DATA ANALYSIS

All concentrations will be reported in parts per billion (ppb). Descriptions of application areas and watersheds sampled will be provided. Analytical results of all samples will be presented in tables.

IX. ESTIMATED TIMETABLE AND NUMBER OF SAMPLES

Sampling is expected to occur periodically through the 1998-1999 study year, and subsequently, intermittent progress reports will be issued to interested parties prior to completion of the final report.

Chemical Analytical Method Development: September 1998
Sampling Period: September 1998 through September 1999
Chemical Analyses: September 1998 through September 1999
Status Progress Report: Fall 1998, Winter 1998, and Spring 1999
Final Report: June 2000

The total number of field water samples anticipated in this study is 36 to 100.

X. RECORDS TO BE MAINTAINED

The following documents will be maintained at the testing facility as described in SOP ADMN005.00 (Supplement 9).

1. All raw data other than those records maintained by the laboratory.
2. The study protocol bearing the original signatures of the study director, sponsor, and quality assurance officers, including amendments and documentation of deviations.
3. All correspondence necessary to reconstruct the study.
4. All progress reports and audits.
5. Documentation of the training and experience of personnel involved in the study.
6. A copy of the final report.
7. All field notes and written observations.

XI. REFERENCES

Barrett, J. 1995. Regional silviculture of the United States. Third Ed., John Wiley and Sons, Inc., New York, New York.

California Department of Forestry. 1979. Forest resources assessment and analysis. Sacramento, California.

Carlson, J. and H. Fiore. 1993. Water monitoring report: 1991 herbicide application projects, El Dorado National Forest. U.S. Forest Service.

Yurok Tribe. 1999. Comments on draft from the Cultural Department of the Yurok Tribe. February, 1999.

SUPPLEMENT 1

Responsibilities of Study Personnel

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
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STANDARD OPERATING PROCEDURE
Personnel Organization and Responsibilities for Studies

KEY WORDS

management; project supervisor; project leader; senior scientist; field coordinator; quality assurance officer; laboratory liaison; statistician; chemist; contact person; GLP; safety; problem resolution

APPROVALS

APPROVED BY: John L. Sanders — DATE: 3/6/97
Management

APPROVED BY: K L Bro — DATE: 3-5-97
EHAP Senior Scientist

APPROVED BY: Randy Segawa — DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: Randy Segawa — DATE: 2-26-97

No previous SOP exists; however, this SOP does supersede the following policy memos:

Goh, K.S. Responsibilities of Field Coordinator for EHAP studies. Memorandum to EHAP Personnel, dated 9/24/93.

Sanders, J. Responsibilities of Project Leaders Regarding Chemical Analysis. Memorandum to EHAP Staff, dated 6/13/88.

Sanders, J. Lab Liaison Personnel and Policy. Memorandum to EHAP Personnel, dated 7/1/87.

STANDARD OPERATING PROCEDURE
Personnel Organization and Responsibilities for Studies

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) defines and discusses the organization and responsibilities of personnel for Environmental Hazards Assessment Program (EHAP) studies. This SOP primarily applies to EHAP field studies, but can also apply to non-field projects.

1.2 Definitions

1.2.1 **Branch** refers to an organizational unit within the Department of Pesticide Regulation (DPR). There are six branches within DPR as shown in Figure 1.

1.2.2 **Protocol** refers to a written document that describes the objectives, personnel, study design, sampling procedures, analytical procedures, data analysis, and schedule for a specific study.

1.3 EHAP Organization

The EHAP is a unit within the Department of Pesticide Regulation (DPR) and provides technical support and monitoring regarding the environmental fate of pesticides. The department and organization of program personnel are shown in Figure 1.

2.0 STUDY ORGANIZATION

Figure 1 shows that the EHAP is organized into groups by function or technical specialty. Personnel are organized into a team for each study. Key study personnel include the Management, Project Supervisor, Project Leader, Senior Scientist, Field Coordinator, Laboratory Liaison, Quality Assurance Officer, Statistician, Chemist and Contact Person. The personnel listed above may not be included in all studies. With certain restrictions, the duties of two or more people may be performed by one person (e.g., the duties of the Project Supervisor and Project Leader may be performed by a single person). The most common personnel organization for a study is shown in Figure 2. The Project Supervisor is selected by the branch chief and/or program supervisor. The Project Leader and other team members are selected by the program supervisor and group supervisors. Selection of all team members should be made

early in the developmental stages of a study to allow them time to understand what management wants to accomplish and to allow sufficient time to prepare for implementing the study.

3.0 PERSONNEL RESPONSIBILITIES

The following personnel have specific responsibilities when assigned to a study.

3.1 Management - Management typically consists of the Assistant Director and Branch Chief and sometimes the Program Supervisor. Management has responsibility for all policy issues, includng the following:

- 3.1.1 determines the objective of a study
- 3.1.2 selects the project supervisor
- 3.1.3 gives final approval for the study protocol, including the budget
- 3.1.4 gives final approval for all SOPs
- 3.1.5 gives approval to any changes in finalized protocols
- 3.1.6 sets study deadlines
- 3.1.7 gives final approval for the study report and any interim memos

3.2 Project Supervisor - The Project Supervisor is typically the supervisor of the Project Leader (i.e., a senior environmental research scientist (supervisor) or the Program Supervisor). The Project Supervisor has overall responsibility for the administrative and technical aspects of the study, including the following:

- 3.2.1 refines the study objectives
- 3.2.2 selects the Project Leader
- 3.2.3 gives general direction to the Project Leader
- 3.2.4 acts as editor-in-chief for review of documents (e.g. protocol, memos, SOPs, report)
- 3.2.5 reviews and approves any changes in finalized protocols
- 3.2.6 supervises administrative tasks (e.g., contracts, purchases, hires)
- 3.2.7 supplies personnel and resources to the Project Leader
- 3.2.8 establishes responsibilities of each team member - consulting with Project Leader
- 3.2.9 facilitates communication with other groups and other branches
- 3.2.10 responsible for safety - determines safety procedures and disseminates hazard communication information - consulting with other DPR branches
- 3.2.11 helps resolve scientific differences of opinion

If the study is conducted under Good Laboratory Practices (GLP), the Project Supervisor is assigned to Management and is also responsible for the following:

3.2.12 establishes a quality assurance unit
3.2.13 assures that test and control substances or mixtures have been tested for identity, strength, purity, stability and uniformity
3.2.14 assures that any deviations from GLP are communicated to the Study Director (Project Leader) and corrective actions are taken and documented

3.3 Project Leader - The Project Leader is typically an environmental research scientist (ERS), associate ERS, or a senior ERS. The Project Leader has primary responsibility for all technical aspects of a study, including the following duties. Some of the following responsibilities may be delegated to other team members.

3.3.1 gathers background information for study - conducts literature search, gathers pesticide use data
3.3.2 identifies personnel needs - sampling, chemical analysis, data analysis
3.3.3 formulates study plan after consulting with team members
3.3.4 writes and follows study protocol and any changes
3.3.5 coordinates protocol dissemination with contact person
3.3.6 communicates with study cooperators - growers, agencies
3.3.7 specifies lab goals through lab liaison - methodology, validation, reporting limits, quality control, turnaround time
3.3.8 interacts with interested parties through the contact person - agencies, public
3.3.9 develops chain of custody form - consults with team members
3.3.10 conducts administrative tasks - contracts, timesheets, purchases, services, budget, expenditures tracking
3.3.11 documents all study activities
3.3.12 obtains necessary permits
3.3.13 determines sampling methodology - consulting with team members
3.3.14 determines sampling schedule - consulting with field coordinator
3.3.15 prepares all pertinent SOPs
3.3.16 trains personnel in study tasks
3.3.17 supervises field sampling and/or data collection
3.3.18 arranges for special facilities - storage, experimental plots
3.3.19 determines sample priorities for lab analysis

3.3.20 reviews and accepts data from the lab
3.3.21 designates samples for reanalysis
3.3.22 reviews laboratory SOPs
3.3.23 supervises data analysis
3.3.24 writes interim progress reports or memos
3.3.25 writes final report - with other team members
3.3.26 coordinates report dissemination with contact person
3.3.27 archives study data
3.3.28 presents results to various audiences

If the study is conducted under GLP, the Project Leader is designated as the Study Director and is also responsible for the following:

3.3.29 corrective actions are taken and documented when necessary
3.3.30 GLP requirements are followed

3.4 Senior Scientist - The Senior Scientist is typically a senior ERS (specialist). The duties of the Senior Scientist and Project Leader cannot be performed by a single person. The Senior Scientist reviews and approves a study for scientific adequacy, including the following specific duties:

3.4.1 gives technical advice to the Project Leader
3.4.2 reviews and approves protocols, memos, SOPs (including lab SOPs) and reports for scientific adequacy
3.4.3 helps resolve scientific differences of opinion
3.4.4 reviews and approves revisions to protocols and SOPs
3.4.5 reviews and approves final report

If the study is conducted under GLP, the Senior Scientist is assigned to the Quality Assurance Unit and assists the Quality Assurance Officer.

3.5 Field Coordinator - The Field Coordinator is typically an associate ERS, ERS, or environmental research assistant from one of the field groups. The Field Coordinator oversees the collection of field samples and has responsibility for field safety. He/She may have more or fewer duties depending on the preference of the Project Supervisor and Project Leader. The Field Coordinator will normally act for the Project Leader in the Project Leader's absence. More than one Field Coordinator may be assigned for very complex studies. The Field Coordinator is normally responsible for the following duties:

3.5.1 decides safety issues under direction of Project Supervisor - the Field Coordinator has the authority to modify or terminate any field activity which threatens the health or safety of field personnel; provides or arranges for safety training
3.5.2 assembles sampling materials
3.5.3 purchases needed materials
3.5.4 arranges transportation and housing
3.5.5 checks and calibrates equipment
3.5.6 assists in developing chain of custody format
3.5.7 assists in coordinating activities with study cooperators
3.5.8 assists in selecting sampling sites
3.5.9 gives advice on sampling methodology
3.5.10 assists in the preparation of SOPs
3.5.11 recommends personnel needs and sampling schedule
3.5.12 prepares sampling materials list
3.5.13 collects and transports samples
3.5.14 coordinates sampling schedule with the Lab Liaison
3.5.15 cleans sampling materials
3.5.16 supervises field sampling in the absence of the Project Leader
3.5.17 assists in the protocol preparation
3.5.18 assists in the report preparation

3.6 Quality Assurance Officer - The Quality Assurance Officer is typically an associate ERS. Duties of the Quality Assurance Officer and Laboratory Liaison are typically performed by one person. The Quality Assurance Officer cannot perform the duties of the Project Leader or Field Coordinator. The Quality Assurance Officer is responsible for documentation and the quality of the laboratory analysis, including the following specific duties:

3.6.1 assists the Project Leader in specifying laboratory methodology
3.6.2 assists the Project Leader in specifying laboratory quality control procedures
3.6.3 reviews and approves EHAP SOPs
3.6.4 maintains copies of protocols and EHAP SOPs
3.6.5 reviews, compiles and disseminates quality control data
3.6.6 notifies Project Leader of analytical problems
3.6.7 initiates lab corrective actions - consulting with Project Leader
3.6.8 arranges the preparation of quality control samples

3.6.9 resolves lab discrepancies
3.6.10 produces method validation and quality control tables for the report
3.6.11 obtains and disseminates laboratory SOPs
3.6.12 reviews laboratory SOPs

If the study is conducted under GLP, the Quality Assurance Officer supervises the Quality Assurance Unit and is responsible for the following:

3.6.13 maintains master schedule of EHAP GLP studies
3.6.14 determines that all known deviations from the protocol or SOPs were authorized and documented
3.6.15 prepares and signs statement of dates of inspection and findings to be included in final report
3.6.16 reviews and approves protocol and final report

3.7 Laboratory Liaison - The Laboratory Liaison is typically an associate ERS. Duties of the Laboratory Liaison and Quality Assurance Officer are typically performed by one person. The Laboratory Liaison is responsible for coordinating activities between EHAP and the chemistry labs, including the following duties:

3.7.1 acts as liaison between the Project Leader and the labs
3.7.2 selects the chemistry laboratories (primary and quality control)
3.7.3 negotiates analytical specifications with the labs (described in SOP QAQC001)
3.7.4 stores and transports samples to the labs
3.7.5 controls timing and quantity of samples delivered to the lab
3.7.6 tracks movement of samples between storage facility and lab
3.7.7 transmits lab data to the Project Leader
3.7.8 administers lab contracts

3.8 Chemist - The Chemist typically works for the Department of Food and Agriculture or a commercial lab, not EHAP. The Chemist is responsible for the pesticide analysis of samples. He/she also gives advice on sampling methodology.

3.9 Statistician - The Statistician is typically an associate ERS. The Statistician is responsible for the design and statistical analysis of the study, including the following specific duties:

3.9.1 determines the study design - consulting with other team members
3.9.2 assists in writing the protocol

3.9.3 reviews and approves the study protocol and any changes
3.9.4 conducts statistical analysis of the study data
3.9.5 assists in writing the final report
3.9.6 reviews final report

3.10 Contact Person - The Contact Person is typically assigned from Program Representation of the Environmental Monitoring Branch. The Contact Person acts as liaison with the public, branches, and agencies that are interested but not participants in the study. His/Her specific duties include the following:

3.10.1 develops interested parties list - consulting with the Project Leader
3.10.2 acts as liaison to public/branches/agencies
3.10.3 disseminates appropriate documents to interested parties
3.10.4 coordinates review of documents with interested parties
3.10.5 assists the DPR communications office with media inquiries
3.10.6 writes executive summary
3.10.7 advises Project Leader on policy and regulatory issues of study

3.11 Other EHAP and DPR Personnel - Designated personnel provide support services. EHAP warehouse personnel provide storage, maintenance, equipment and transportation upon request. EHAP laboratory facilities are available for soil characterization and other analyses upon request. A number of people within and outside of EHAP provide special computer services such as programs, databases, modeling, geographic information systems, or graphics upon request. The Worker Health and Safety, and Medical Toxicology Branches can provide information on toxicity, safety precautions as well as medical monitoring upon request. These support personnel may not be available for all studies and should be requested through the Project Supervisor or the appropriate Group Supervisor.

4.0 PROBLEM RESOLUTION

Technical items that are not specified here are the responsibility of the Project Leader. Both the Project Leader and Senior Scientist should agree on all technical issues. The Project Supervisor is responsible for resolving any disagreements. Administrative, policy or other items not specified here are the responsibility of the Project Supervisor.

5.0 SAFETY

Personnel safety is of primary importance at all times. The Project Supervisor and Field Coordinator have primary responsibility for safety. However, all team members must follow correct safety procedures. Approval for changing the protocol or a SOP should be sought whenever possible, but may not be possible if an imminent danger exists. A study should always be conducted in a safe manner, no matter what the protocol or SOP specifies. Document all changes in the protocol or SOP.

In the absence of the Field Coordinator, the ranking field group person has primary responsibility for safety while working in the field.

6.0 STUDY-SPECIFIC DECISIONS

Management, Project Supervisor and Project Leader are responsible for the following study-specific decisions:

6.1 Selection of study personnel
6.2 Responsibilities of each team member

7.0 REFERENCES

Goh, K.S. Responsibilities of Field Coordinator for EHAP studies. Memorandum to EHAP Personnel, dated 9/24/93.

Sanders, J. Responsibilities of Project Leaders Regarding Chemical Analysis. Memorandum to EHAP Staff, dated 6/13/88.

Sanders, J. Lab Liaison Personnel and Policy. Memorandum to EHAP Personnel, dated 7/1/87.

APPENDICES

Figure 1. Department of Pesticide Regulation Personnel Organization

Figure 2. EHAP Study Personnel Organization

SUPPLEMENT 2

Depth-integrated, Equal Width-increment Method for Sampling Surface Water

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE
Equal-Width-Increment Sampling of Surface Waters

KEY WORDS

Field sampling; water quality; discharge; contamination

APPROVALS

APPROVED BY: _____ DATE: 2/13/98
Management

APPROVED BY: _____ DATE: 2/5/98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 2/9/98
EHAP Quality Assurance Officer

PREPARED BY: Kevin P. Bennett DATE: 2/5/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

1.0 INTRODUCTION

1.1 Purpose

This Standard Operation Procedure (SOP) discusses the specific procedure for sampling surface water using the equal-width-increment (EWI) method. A cross-sectional depth-integrated sample obtained by the EWI method gives a sample volume proportional to the amount of flow at each of several equally spaced verticals in the cross section. This document gives instruction on A) determining the number of verticals, B) determining a transit rate, and C) collection of a sample volume.

1.2 Definitions

In the context of this SOP, surface water is defined as all inland waters, excluding groundwater, which are suitable for use as a source of domestic, municipal, or agricultural water supply and which provide habitat for fish and wildlife.

2.0 MATERIALS

2.0.1 D-77 Sampling Unit
2.0.2 Bridge Board/Crane and Reel
2.0.3 5/16" Nozzle/Cap Assembly
2.0.4 3-liter Teflon® Bottle
2.0.5 Tag-line or Tape Measurer
2.0.6 Composite Sample Container

3.0 PROCEDURES

Instructions included here are modified from the following document: Edwards, T.K. and D.G. Glysson. Field Methods for Measurement of Fluvial Sediment, U.S. Geological Survey Open-File Report 86-531. pp. 61-64.

3.1 Number of Verticals

3.1.1 Looking downstream, measure the perpendicular distance from the left edge of water to the right edge of water.

3.1.2 Visually inspect the stream from bank to bank, observing the velocity and depth distribution as well as apparent distribution of sediment in the cross section.

3.1.3 Determine the size of the interval that represents approximately 10% of the flow at that part of the cross section where the "unit width discharge" is highest (generally the deepest, fastest section). This increment must be used for the entire cross section. Typically, this works out to be from 10 to 20 increments for streams 5 feet wide.

3.1.4 For example, if the stream width determined from the tag-line or tape measurer is 160 feet and the width of each increment was determined to be 16 feet, then the number of verticals required is 10. The sample station within each width increment is located at the center of the increment. In this example, the first sampling station would be at 8 feet from the bank nearest the initial point for width measurement. The verticals are then spaced 16 feet apart, resulting in sample stationing at 24, 40, 56, 72, ... and 152 feet of width.

3.1.5 If stream is < 5 feet wide, divide into as many equal increments as possible, with the minimum increment width being 3 inches.

3.2 Transit Rate

3.2.1 Determine the vertical increment that contributes the greatest flow to the stream channel (the fastest and deepest). Determine the mean vertical velocity using a current meter. The bronze D-77 operates at velocities up to 7.2 feet per second, and the aluminum D-77 to 3.3 feet per second.

3.2.2 Set up D-77 sampling unit at vertical determined from step 3.2.1 and lower unit until the bottle nozzle is just above the surface of the stream.

3.2.3 Using a stopwatch, determine the rate (cranks/second) and number of transits that it takes to fill the sampling bottle without overfilling. (A bottle is overfilled when the water surface in the bottle is above the nozzle or air exhaust with the sampler held level.) Several iterations will be required to determine the final transit rate, and this transit rate must be used at each vertical. It is possible to sample at two or more verticals using the same bottle if the bottle is not overfilled.

3.3 Sample Collection

3.3.1 Set up D-77 sampling unit (with crank and gauge) at first vertical station and lower until the bottle nozzle is just above the water surface and reset depth gauge to zero.

3.3.2 Using the transit rate determined in step 3.2.3, lower unit into stream and raise to surface once bottom is felt. The movement of the sampling unit throughout the water column must be constant with minimal disturbance of the stream bottom. Continue across stream to its far edge, depositing vertical samples into a composite sample container. Complete necessary transects, until desired volume is obtained. **Note: *An equal number of transits must be made at each vertical.***

4.0 STUDY-SPECIFIC DECISIONS

Study specific information should be included in the study protocol, a separate document describing a specific study.

5.0 REFERENCES

Standard Operating Procedure: ADMN002.00. 1996. Personnel organization and responsibilities for studies. California EPA, Department of Pesticide Regulation, Environmental Hazards Assessment Program. Sacramento, CA.

SUPPLEMENT 3

Splitting Water Samples

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE

Instructions for Splitting Water and Rinsing the Geotech® Dekaport Splitter and Splitting Equipment

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KEY WORDS-
Splitter; rinse; cross-contamination

APPROVALS

APPROVED BY: _____ DATE: 6/22/98
Management

APPROVED BY: _____ DATE: 6/1/98
EHAP Senior Scientist

APPROVED BY: _____ DATE: 6/18/98
EHAP Quality Assurance Officer

PREPARED BY: _____ DATE: 6/18/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE

Instructions for Splitting Water and Rinsing the Geotech® Dekaport Splitter and Splitting Equipment

---

1 .O INTRODUCTION

1.1 Purpose

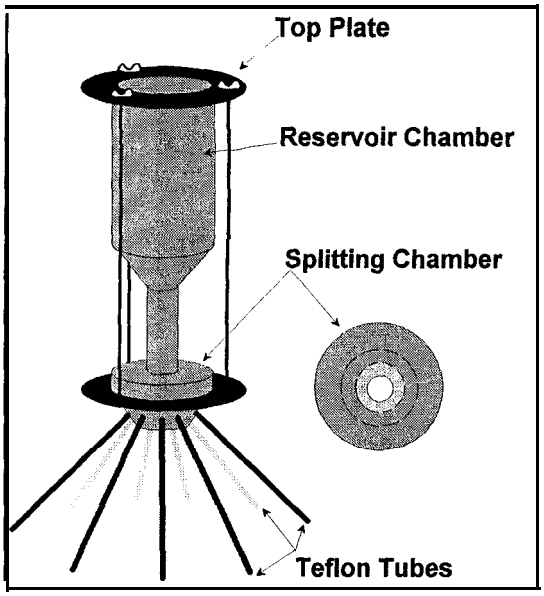
To ensure effective mixing and splitting of a surface water sample when various paired analyses are to be performed and to describe proper cleaning of equipment to prevent cross-contamination.

1.2 Scope

This document will provide specific instructions for splitting surface water samples and rinsing the splitter.

2.0 MATERIALS

2.1 Large glass jars, stainless steel milk can or container large enough to hold sample water that will be split
2.2 Water sample
2.3 Geotech® 10 port splitter
2.4 Sample containers
2.5 Stainless steel buckets, funnel
2.6 Chain of Custody records
2.7 Latex gloves
2.8 Deionized water (3 or more gallons)
2.9 Leveler
2.10Large Plastic Bags



3.0 PROCEDURES

Samples should be transported in a glass or stainless steel container on wet ice (4°C), from collection site to the site where splitting will occur.

3.1 Splitting Procedure

3.1.1 Place the pre-cleaned (see EQWA001) Geotech® dekaport water splitter on level ground. Make sure all splitter water spouts are level to ensure

a fairly even water flow. Place a level across the top of the splitter to ensure that it is level.

3.1.2 Set up to a maximum of 10 sample containers under each Teflon port. If exactly 10 l-liter sample containers (or smaller) are required, use one port per container. If less than 10 samples are required, use fewer ports, or two tubes can be placed in each container. However, all bottles must be treated the same way each time a sample of water is to be split so that each sample contains the same amount of water and sediment. When there are more than ten sample bottles, e.g. 15, then divide the splitter spouts between two buckets and pour the water through the splitter. Then pour the water from one bucket through the splitter into half the sample bottles, then pour the water from the other bucket through the splitter into the remaining bottles. Collect excess water from unused spouts in an uncontaminated bucket or preferably a container used to hold the water sample originally (e.g., a Teflon sampling bottle). This water can be poured through the splitter again to fill the bottles completely.

3.1.3 Immediately before pouring collected sample water into the splitter, mix water inside a glass or stainless steel sample collection container to suspend the sediment. If more than one container was used to collect the sample, mix the separate containers together in a larger container such as a stainless steel milk can. Prior to completely pouring the remainder of the sample water out of the sample containers into the milk can, or into the splitter directly, swirl the water one last time to ensure that all the remaining sediment stays with the sample water and not at the bottom or along the sides of the container.

3.1.4 While pouring the sample water through the splitter, keep the water level near the top of the reservoir chamber so that as much head pressure is maintained as possible to ensure even flow through the spouts. Again, prior to pouring out the last of the sample water, swirl to get the sediment suspended.

3.1.5 Cap all sample containers and rinse the splitting equipment as described below.

STANDARD OPERATING PROCEDURE
Instructions for Splitting Water and Rinsing the Geotech® Dekaport Splitter and Splitting Equipment

3.2 Rinsing Procedure

3.2.1 If the splitting is conducted at a facility, rather than out in the field, rinse the splitter and all equipment thoroughly with tap water, then proceed to the next step. If splitting is conducted in the field, rinse the splitter and all equipment with deionized-distilled water and add one rinse (see 3.2.3 below).

3.2.2 Rinse the splitter and associated equipment after splitting any water sample by pouring approximately 2 L of deionized water into either the milk can or steel bucket used in the splitting procedure. Then swirl the water to wash out residues. Pour that same water into the next piece of equipment (such as another bucket that was used for splitting), and again swirl the water and pour into another piece of equipment. This continues through all the equipment and ends by pouring the deionized water through the splitter.

3.2.3 This process is completely repeated from start to finish three times, each time with new, uncontaminated 2L volume of deionized water. If initial rinse did not include tap water, as in 3.2.1, then rinse with deionized water once more.

3.2.4 Cover all containers and the splitter with clean plastic bags between uses.

SUPPLEMENT 4

Packaging and Transporting Samples

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
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Sacramento, California 95814

STANDARD OPERATING PROCEDURE

Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

---

KEY WORDS-
Ice chest, sample, ice, temperature

APPROVALS

APPROVED BY: _____ DATE: 9/25/99
Kean S. Goh, Management

APPROVED BY: _____ DATE: 9/7/99
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APPROVED BY: _____ DATE: 9/7/99
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REVISED BY: _____ DATE: 9/2/99
DeeAn Jones, Environmental Research Scientist

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory

---

1.0 INTRODUCTION

1.1 Purpose

To ensure that samples are adequately packed in the field to avoid breakage and that samples are stored at the appropriate temperature for each media.

1.2 Scope

This document will provide specific instructions for packing and transporting samples after they have been collected. For instructions on how to package sampling materials prior to collection, see Standard Operating Procedure QAQC005.00.

2.0 MATERIALS

2.1 Ice chests
2.2 Wet ice or blue ice for cooling water or vegetation samples
2.3 Dry ice for cooling soil, air, or vegetation samples
2.4 Appropriate packing material for sample containers (ex: styrofoam 6-packs for quart jars and 1 L Amber bottles)
2.5 Hobo® Temp data logger or Min/Max Temperature recorder
2.6 Bubble plastic or other packaging material
2.7 Duct tape or packing tape
2.8 Permanent black marker
2.9 White label tape

3.0 PROCEDURES

3.1 SAMPLE TRANSPORT FROM THE FIELD TO THE WAREHOUSE OR LABORATORY

Before leaving the warehouse (sometime prior to sample collection), an ice chest should be filled with the appropriate ice (wet, dry, blue). This is to ensure that the samples are chilled immediately after collection. If the study is conducted under Good Laboratory Practices, a Hobo® Temp data logger or Min/Max Temperature recorder should be placed in each ice chest. Instructions for operating a Hobo® Temp data logger are found in Standard Operating Procedure EQOT001.01.

3.1.1 Place samples in styrofoam holders or other containers in ice chests immediately after sampling in the field or removal from storage refrigerators or freezers at an Environmental Hazards Assessment Program warehouse facility.

3.1.2 Surround the samples with sufficient ice to chill to the appropriate temperature. For **water samples** and **vegetation to be analyzed for internal and/or dislodgeable residue**, use wet ice or blue ice to chill the samples to 4°C. For **air**, **soil**, and **vegetation to be analyzed for total residue** use dry ice to chill the samples to -10°C to -70°C. It is preferable to maintain total pesticide residue samples at -70°C. If dry ice is not available, use any form of refrigeration in the following order of desirability: 1) freezer, 2) refrigerator, 3) blue ice, 4) wet ice (Sava, 1994). If the study is conducted under Good Laboratory Practices, the time and date the samples were placed in the ice chest should be recorded in the field notebook.

3.1.3 Check the samples often, making sure there is enough ice to maintain the required temperature. Add more ice when necessary, and drain off water as wet ice melts.

3.2 ADDITIONAL SHIPPING PROCEDURES

3.2.1 Pack samples securely by either adding packing material or wrapping containers in bubble plastic in order to prevent breakage.

3.2.2 Chain of custody (COC) records must accompany samples at all times and should be filled out according to Standard Operating Procedure ADMN006. Secure COCs in plastic bags and tape to the inside of the ice chest lid.

3.2.3 Using duct or packing tape, wrap the ice chest twice to seal the opening. This will alert the sample custodians to whether or not the ice chest has been tampered with.

3.2.4 If the ice chest is not already labeled, use the permanent marker and label tape to address the package to the appropriate destination. Note: Certain shipping companies may require a specific label to be used. Also, check with the airline or shipping company for any restrictions, including type of ice to be used.

3.3 RECEIVING

Samples that have been shipped to the West Sacramento warehouse, will be received by a sample custodian. This custodian will follow Standard Operating Procedure QAQC003.01 for check-in and check-out methods. Additionally, the custodian will notify the EHAP QA officer and project leader of any samples broken during transport and record the condition on the corresponding COC.

4.0 REFERENCES

Sava, R. 1994. Guide to Sampling Air, Water, Soil, and Vegetation for Chemical Analysis. Department of Pesticide Regulation - EHAP report EH 94-04. Sacramento, California.

SUPPLEMENT 5

Sample Tracking Procedures

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
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STANDARD OPERATING PROCEDURE
Sample Tracking Procedures

KEY WORDS

Sample Tracking, Sample Tracking Database, Chain-of custody, Sample

APPROVALS

APPROVED BY: John S. Sanders DATE: 3/6/97
Management

APPROVED BY: H. L. Blanco DATE: 3-5-97
EHAP Senior Scientist

APPROVED BY: Randy Seaman DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: Andrea Hoffman DATE: 2-26-97

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) discusses sample check-in and check-out procedures; the recording of chemistry data; sample disposal procedures; and the Sample Tracking Database.

1.2 Definitions

A **sample** is any environmental substance collected and analyzed for chemical content.

Chain-of-custody is a record describing in detail all pertinent information specific to each sample, including dates and signatures of persons handling the sample.

Sample Tracking Database is a relational database designed in Microsoft Access to trace a sample from the time it is checked into the storage facility until the sample is submitted to a laboratory for analysis or disposed of after a study is completed.

2.0 SAMPLE TRACKING

2.1 Sample Tracking Codes

Sample tracking codes are abbreviations for fields in the database that refer to specific information about each sample. The study number in combination with the sample number is identified as the key field and all information specific to the sample is referenced by the following codes back to the key field.

SAMPLE CODES:

P= Primary	R= Replicate	B= Backup	FB= Field Blank
* = Split	S= Spike	BG= Background	BM= Blank Matrix
A= Acidified	U= Unacidified	RB= Rinse Blank	

STORAGE LOCATION CODES refer to the storage location of each sample at the storage facility.

F= Fresno	R= Refrigerator	SRI 0= Sacramento Refrigerator #I 0
R= Riverside	F= Freezer	SFO7= Sacramento Freezer #07
S= Sacramento	A= Air Temp.	D= Deep Freeze
W= Warehouse	L= Lab	

SAMPLE TYPE CODES refer to the sample matrix collected.

FRU= Fruit	DVEG= Dislodgeable Vegetation	TWG= Twigs
SOI= Soil	SSS= Stainless Steel Sheets	EXT= Extract
WAT= Water	LOV= Lo-Vol	STD= Standard
VEG= Vegetation	HIV= Hi-Vol	SUR= Surrogate
SED= Sediment	FILT= Filtrate	TUR= Turf
TAN= Tank	KIM= Kimbie	SAN= Sand
AIR= Air	TRP= Air Cassettes	BRA= Branch

SAMPLE CONTAINER CODES refer to the type of container each sample is placed in during storage.

QMSJ= Quart Mason Jar	1 LAMBR= 1 Liter Amber Bottle
PMSJ= Pint Mason Jar	HPMSJR= Half Pint Mason Jar
PBAG= Plastic Bag	HIVJAR= Hi-Vol Jar
FOIL= Aluminum Sheets	P500mL= Plastic Bottle (500 mL)
CAS= Air Cassettes	1 LPC= 1 Liter Polycarb. Bottle
lLPP= 1 Liter Polyprop. Container	VIAL= Small Standard Vial

500mLPC= 500mL Polycarb. Container
250mLAMBR= 250mL Amber Bottle
500mLAMBR= 500mL Amber Bottle
500mLHDPP= 500mL High Density Polyprop.

LABORATORY CODES refer to the specific laboratory each sample is shipped to for analysis.

QUAN= Quanterra Laboratory	CDFA= CA Dept. of Food & Agr.
ATL= Aquatic Toxicology Lab	CDFG= CA Dept. of Fish & Game
FMC= FMC Corporation	ALTA= ALTA Analytical Laboratory
ZEN= Zeneca Ag Products	VAL= Valent Dublin Laboratory
APPL= Ag and Priority Pollut Labs	MOR= Morse Laboratories Inc.
NCL= North Coast Labs	UCD= University California Davis
FRES= Fresno Soils Lab	WSAC= W. Sacramento Soils Lab

ANALYSIS TYPE refers to the type of test method to be performed on each sample.

C= Chemical	F= Tracer	E= Elisa
0= Organic	P= pH	M= Moisture
T= Texture	B= Bulk Density	V= Various

2.2 Sample Check-in Procedures

All samples received at the storagefacility are immediately put in a refrigerator or freezer depending on the matrix specific storage requirements. The field crew fills out a two-part check-in sheet (Figure A) using the sample tracking codes listed in section 2.1.

The check-in sheet must be complete in order to properly track environmental samples. The following is a description of each key component of the check-in sheet.

Project ID: The study number or name.
Date Received: The date the sample was received from the field crew.
Checked-in by: The initials of the person who fills out the check-in sheet.
Remarks: List any additional or neccessary information regarding the samples listed on the check-in sheet.
EHAP Sample No.: The number assigned to a labeled sampling container.
Sample Code: List sample code (Section 2.1 for codes).
Date Sample Collected: Note the sample collection date.
Sample Type: Specify the type of sample collected (Section 2.1).
Container Type: What the sample is stored in (Section 2.1).
Analysis Type: The type of analysis the sample is intended for (Section 2.1).
Analysis: List the type of chemical the sample is to be analyzed for.
Comment: Space provided for additional information regarding individual samples.
Date/Logged in by: The date and person who enters information into the Sample Tracking Database.
Storage Location: List where the sample is being stored (Section 2.1).

After the check-in sheet is completed, each field sample is compared against its corresponding chain-of-custody (COC), then signed and dated by the sample custodian receiving the sample. The white and yellow copies of the each COC is removed and sent with its correpsonding field sample to the laboratory. The pink copy is used to enter the information into the Sample Tracking Database. The pink copy is then sent to the Project Leader. Any remaining samples held at the storage facility are stored under thieir required storage conditions with the white and yellow copies of their corresponding COCs.

2.3 Sample Check-out Procedures

A two-part check-out sheet is filled out for any sample leaving the storage facility (Figure B). The check-out sheet must be complete in order to properly track environmental samples leaving the storage facility.

The check-out sheet is similar to the check-in sheet but differs in three components.

> **Date Delivered:** The date the sample is taken to the laboratory.
> **Checked-out by:** The initials of the person filling out and transporting the sample to the laboratory.
> **Laboratory Delivering to:** Specify the destination code for the sample scheduled for analysis (Section 2.1).

A pink copy of the check-out sheet, and white and yellow copy of each COC are sealed in a plastic bag and accompany samples transported to the laboratory. The samples are then placed in ice chests and cooled to their required temperatures using blue ice, wet ice or dry ice. Ice chests are sealed with tape and labelled with the date and inititals of the sample custodian using a permanent black marker. The white copy of the check-out sheet is retained by the QA/QC officer and is also used to enter information into the Sample Tracking Database.

2.4 Chemistry Results

After results are received from the laboratory, the laboratory sample number, extraction and analysis date for each sample are entered into the Sample Tracking Database using the appropriate Microsoft Access query.

2.5 Sample Disposal

After each study is completed and with the approval of the Project Leader, all remaining samples stored in the storage facility may be disposed of by the sample custodian. A two-part Sample Disposal Sheet is completed and includes information similar to the check-out sheet (Figure C). This information is then entered into the Sample Tracking Database using the appropriate Microsoft Access query. The white copy of the Sample Disposal Sheet is retained by the QA/QC officer while the yellow copy is used to enter the information into the database.

3.0 Sample Tracking Database

All the information reported on the check-in, check-out, chemistry result, and sample disposal sheets is entered in the Sample Tracking Database using tables in Microsoft Access. Queries, forms and reports are designed specifically for each study to access fields for summarizing data.

3.1 Computer Generated Backups

Daily and weekly backups are conducted using Norton software and a tape drive. Diskettes are also used as a source for daily backup of individual study files.

STATE OF CALIFORNIA

DEPARTMENT OF PESTICIDE REGULATION

ENVIRON. MONITOR. & PEST MGT.
SACRAMENTO SOILS LABORATORY
3971 COMMERCE DRIVE, SUITE D
WEST SACRAMENTO, CA 95691
(916) 322-3082

SAMPLE CHECK-IN SHEET
30-007 (4/90)

Today's Date: _____

Project ID (Study no.): _____

Logged in by: _____
(key data entry person)

Date Received: _____

Storage location: _____
(see # on outside of storage)

Checked- in by : _____

Remarks:

EHAP Sample No.	Sample Code	Date Sample Collected	Sample Type	Container Type	Analysis Type	Analysis	Comment

STATE OF CALIFORNIA

DEPARTMENT OF PESTICIDE REGULATION

SACRAMENTO SOILS LABORATORY
3971 COMMERCE DRIVE, SUITE D
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(916) 322-3082

SAMPLE CHECK-OUT SHEET
30-008 (4/90)

Today's Date: _____

Project ID (Study no.): _____

Logged out by: _____
(key data entry person)

Date Delivered: _____

Storage location: _____
(see # on outside of storage)

Checked-out by: _____

Laboratory Delivering to: _____

Remarks:

EHAP Sample No.	Sample Code	Date Sample Collected	Sample Type	Container Type	Analysis Type	Analysis	Comment

California Dept. of Pesticide Regulation
Environmental Hazards Assessment Program
3971 Commerce Drive, Suite D
West Sacramento, CA 95691
(916)322-3082

Today's Date: _____

Sample Disposal Sheet

Project ID (Study no.): _____ Disposed by: _____

Date Disposed: _____ Storage location: _____

==========

Remarks:

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EHAP Sample #	Sample Code	EHAP Sample #	Sample Code	EHAP Sample #	Sample Code	EHAP Sample #	Sample Code

SUPPLEMENT 6

Chemistry Laboratory Quality Control

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
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STANDARD OPERATING PROCEDURE
Chemistry Laboratory Quality Control

KEY WORDS

QC; method detection limit; MDL; reporting limit; RL; confirmation; verification; AB 2021; method development; method validation; storage stability; split; spike; blank; laboratory specifications

APPROVALS

APPROVED BY: John S. Sanders — Management — DATE: 7/31/95

APPROVED BY: Heinz L. Blum — EHAP Senior Scientist — DATE: 7/31/95

APPROVED BY: Randy Segawa — EHAP Quality Assurance Officer — DATE: 7/28/95

PREPARED BY: Randy Segawa — DATE: 7/28/95

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Chemistry Laboratory Quality Control

1.0 INTRODUCTION

1.1Purpose

This Standard Operating Procedure (SOP) discusses the chemistry laboratory quality control (QC). These guidelines describe method development as well as continuing quality control procedures that should be followed for all Environmental Hazards Assessment Program (EHAP) studies.

1.2 Definitions

1.2.1 **AB 2021 Confirmation** refers to the detection of a pesticide in at least two discrete well samples.

1.2.2 **AB 2021 Verification** refers to analysis "by a second analytical method or a second analytical laboratory approved by the department." Confirmation and verification are defined and discussed at length (particularly in the AB 2021 context) in the memorandum from Randy Segawa to Kean Goh, dated 11/22/93.

1.2.3 **Analytical Confirmation** refers to an analyte that has been unequivocally identified. For an analytical method that is nonspecific (e.g., gas chromatography with a flame photometric detector) analytical confirmation requires a second analysis that has a change in both the separation and detection principle. Except for AB 2021 projects, an analytical method that is specific (e.g., massspectrometry) meets the analytical confirmation criterion and a second analysis is not required. AB 2021 requires a second analysis even if the primary method is specific.

1.2.4 **Blank** refers to a sample with no detectable amount of pesticide. Blanks are used to check for contamination or to prepare QC samples (e.g., **blank-matrix, reagent. blank,** and **field blank** samples).

1.2.5 **Blind Spike** refers to a blank-matrix sample which has been spiked and submitted to the lab disguised as a field sample.

1.2.6 **Extract** refers to the final solvent which contains the pesticide residue.

1.2.7 **Extraction Set** refers to a single group of samples extracted and processed at the same time.

1.2.8 **Instrument Detection Limit (IDL)** is 1 - 5 times the signal-to-noise ratio depending on the analytical method.

1.2.9 **Method Detection Limit (MDL)** refers to the USEPA definition (40 CFR, Part 136, Appendix B). "The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix...."

1.2.10 **Reporting Limit (RL)** is 1 - 5 times the MDL depending on the analytical method and matrix. The MDL can vary from sample to sample because of matrix effects. Ideally, the RL will not change, will be set high enough to account for matrix effects, yet low enough to be useful.

1.2.11 **Spike** refers to a known amount of pesticide added. These QC samples are used to check the precision and accuracy of a method.

1.2.12 **Split** refers to one homogeneous sample divided into several aliquots, with the different aliquots analyzed by different laboratories. These QC samples are used to check the specificity and precision of a method.

1.2.13 **Standard** refers to the laboratory analytical standard.

2.0 GENERAL PROCEDURES

These guidelines are meant to be a starting point; a specific study may require more or less QC than is given here. The procedures outlined here are the QC measures which should be reported. Performing other QC procedures such as frequency of standard injections and calibrations are left to the chemist's discretion.

2.1 General Method Development

Many times the method development will be a negotiation between the project leader and the laboratory. The project leader can suggest some method perfomance goals (e.g., specificity, reporting limit, etc.), but the goals need to be balanced with laboratory cost and time constraints. The, method performance should be consistent with the study objectives.

2.1.1 *Standard* - Standard solutions should be validated prior to use by checking for chromatographic purity or verification of the concentration using a second standard prepared at a different time or obtained from a different source.

2.1.2 Method Detection Limit Determination - The MDL is determined by the USEPA method (40 CFR, Part 136, Appendix B). The complete procedure is given in Appendix 1. Briefly, the MDL is determined by analyzing at least 7 low-level matrix spikes (generally 1 - 5 times the IDL) and performing the following calculation:

$$MDL = t \times S$$

where:

t = Student's t value for 99% confidence level (l-tailed) and n-l degrees of freedom
S = standard deviation

2.1.3 Reporting Limit Determination - The RL is determined by the chemist and set at 1 - 5 times the MDL depending on the matrix and instrument.

2.1.4 Method Validation - At the onset of a study, an acceptable range of spike recoveries will be established. This range will be established by analyzing blank-matrix spike samples. Two to five replicate analyses at two to five different spike levels will be used to determine the mean percent recovery and standard deviation. Number of replicates and spike levels will be chosen by the project leader. Warning limits will be established at the mean percent recovery plus/minus 1 - 2 times the standard deviation. Control limits will be established at the mean percent recovery plus/minus 2 -

3 times the standard deviation. Any subsequent spiked samples outside the control limits may require the set of samples associated with that spike to be reanalyzed.

2.1.5 Storage Stability - Storage stability needs to be evaluated on a case-by-case basis, so no specific test design is specified. However, in general the test should be run for the longest anticipated holding period, with at least four sampling intervals and two replicate samples at each sampling interval. Other factors may also need to be incorporated into the storage stability tests, such as pH, temperature, and container type. The project leader is responsible for specifying the design of the storage stability test.

2.2 General Continuing QC - These analyses are to be done by the main lab on a continuing basis. Each extraction set should consist of 5-20 actual samples. Exact frequency of QC analyses and spike levels are chosen by the project leader.

2.2.1 Reagent Blanks - 1 - 2 per extraction set

2.2.2 Blank-Matrix Spikes - 1 - 3 per extraction set

2.2.3 Analytical Confirmation - 0 to 100% (normally 10%) of positive samples confirmed

2.2.4 Split Matrix Samples - 0 to 100% (normally 10%) of the actual samples should be split into two aliquots, one aliquot analyzed by the main lab, and one by the QC lab. For studies that cannot have actual samples split or for which only a few positives are anticipated, blind spike samples may be used.

2.2.5 Blind Spikes - 0 to 100% (normally 10%) of the actual samples should be accompanied by laboratory-spiked samples disguised as real samples. These should be done only for matrices that can be accurately spiked.

2.3 Optional Continuing QC - The following analyses should be considered but may not be routinely performed unless specified by the project leader.

2.3.1 Internal Standard - a chemical not expected in the samples can be spiked into all samples or extracts. This is particularly useful for quantifying mass spectrometry data.

2.3.2 Replicate Sample Analyses - analyzing multiple aliquots of a single sample will give a better estimate of the method precision.

2.3.3 Replicate Extract Analyses - multiple analyses of a single extract will give a separate estimate of the precision of the extraction and analysis processes.

2.3.4 Split Extract Analyses - analyzing a single extract with more than one lab is useful for checking discrepancies between laboratories.

2.3.5 Reference Material - a stable sample that contains the analyte(s) of interest and has been analyzed many times so that the concentration(s) are known. Analysis of this material may give a better estimate of the methods accuracy than spiked samples. Also useful for method development.

2.3.6 Standards Exchange - exchanging analytical standards between the primary and QC lab is useful for checking discrepancies in split samples.

3.0 WELL WATER STUDY QC PROCEDURES

3.1 Well Water Study Method Development - The general method development procedures should be used.

3.2 Well Water Study Continuing QC - The following specific continuing QC should be used in place of the general continuing QC:

3.2.1 Reagent Blanks - 1 to 2 per extraction set

3.2.2 Blank-Matrix Spikes - 1 to 3 per extraction set

3.2.3 AB 2021 confirmation and verification - at least one additional sample' from the same well must be analyzed by a second lab or a second method for each positive sample. AB 2021 confirmation requires positive detection in at least 2 discrete samples and verification with a second lab or a second method:

3.2.4 Blind Spikes - 1 blind spike should be submitted for every 3 - 50 well samples.

3.2.5 Field Blanks - 1 field blank should be collected at each well, but analyzed only if the well sample is positive.

4.0 AIR STUDY QC PROCEDURES

4.1 Air Study Method Validation (trapping efficiency) - In addition to the general procedures, the trapping efficiency should be determined. This normally involves collecting a series of 2-stage air samples. The top stage sampling tube contains glass-wool and is spiked. The bottom stage consists of the normal sampling tube. The 2-stage sample is placed on an air sampler and run for the appropriate amount of time. Both stages are then analyzed to determine the proportion of the spike trapped in the bottom stage. The test should consist of two to five replicate analyses at two to five spike levels. Samplers should run for various lengths of time, if necessary. To determine the precision of the spiking technique, five sample tubes with glass wool should be spiked and analyzed. Oxidation products should also be analyzed to determine the rate of conversion. Exact test specifications are chosen by the project leader.

4.2 Air Study Continuing QC - In addition to the general procedures, one reagent spike should be analyzed with each extraction set. The air sampling matrix will occasionally give an enhanced detector response.

In general, it is not possible to split air samples, so split matrix analyses are not usually done.

5.0 CALCULATIONS

5.1 Calculating the Method Detection Limit - The MDL is determined by performing the following calculation:

$$MDL = t \times S$$

where:

t = Students t value for 99% confidence level (l-tailed) and n-l degrees of freedom
S = standard deviation

5.2 Calculating Warning and Control Limits - The method validation data are used to set warning and control limits. Warning limits will be established at the mean percent recovery plus/minus 1 - 2 times the standard deviation. Control limits will be established at the mean percent recovery plus/minus 2 - 3 times the standard deviation. Any subsequent spiked samples outside the control limits may require the set of samples associated with that spike to be reanalyzed.

6.0 REPORTING REQUIREMENTS

These reporting requirements pertain only to the QC data. There may be other reporting requirements specified in the EHAP Analytical Laboratory Specifications Form (Appendix 2).

6.1 Reporting Method Development Results - The following should be reported by the lab to the EHAP QA officer prior to the start of any field sample analyses: the spike level and concentration detected for each sample of the MDL determination, the method validation, and the storage stability. The EHAP QA officer will review, summarize and submit the data to the project leader.

6.2 Reporting Continuing QC Results - The following QC results should be reported by the lab to the EHAP QA officer on a continuous basis: the concentration of all blanks, the concentration detected for all spikes, the amount added for all spikes. Any spiked samples outside the control limits mav require the set of samples associated with that spike to be reanalyzed. The **EHAP** QA officer will

review, summarize and submit the data to the project leader. In addition, the project leader may request to be notified if any problems arise during the course of chemical analysis.

6.3 Reporting Sample Results - The laboratory should not use any spike or blank data to adjust the **field** sample results, unless specified by the project leader. Any adjustments should be made by EHAP personnel.

7.0 STUDY-SPECIFIC DECISIONS

The project leader is responsible for the following specific decisions for each individual study. These decisions must be made for both the primary lab and the QC lab, if one is used. All decisions should be given to the EHAP QA officer who will document the decisions and transmit them to the lab using the EHAP Analytical Laboratory Specifications Form.

7.1 Method performance goals - reporting limit, specificity, precision, accuracy, sample size, time to complete analysis, etc.

7.2 Number of MDL spike samples

7.3 Method validation spike levels and number of replicates

7.4 Warning and control limit criteria (1 - 3X standard deviation)

7.5 Storage stability test design

7.6 Number or frequency of continuous QC spike analyses

7.7 Concentration of continuous QC spike samples

7.8 Number or frequency of analytical confirmation

7.9 Number or frequency of split analyses

7.10 Use, selection and concentration of an internal standard

7.11 Number or frequency of replicate sample analyses

7.12 Number or frequency of blind spike analyses

7.13 Concentration of blind spike samples (also select analyte(s) if multi-residue method)

7.14 Number or frequency of replicate extract analyses

7.15 Number or frequency of split extract analyses

7.16 Number or frequency of standard reference material analyses

7.17 Method of AB 2021 verification - 2nd lab or 2nd method

7.18 Trapping efficiency test design

7.19 Number or frequency of reagent spike analyses

8.0 REFERENCES

California Department of Pesticide Regulation. 1988. Chemistry Laboratory Quality Control Guidelines. Environmental Hazards Assessment Program.

Segawa, R. 1993. AB 2021 Confirmation and Verification Policy. Memorandum to Kean Goh, dated November 22, 1993. Environmental Hazards Assessment Program.

APPENDIX 1 - U.S. EPA Method Detection Limit Determination

APPENDIX 2 - Analytical Laboratory Specifications

APPENDIX 1

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a signifi-

cantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right]$$

$$S = (S^2)^{1/2}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha\,=\,0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha\,=\,.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ i-\alpha\,=\,.99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which

affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

Project No. _____ Lab _____
Lab Project Manager _____ Phone _____
Project Chemist _____ Phone _____
EHAP Project Manager _____ Phone _____
EHAP Lab Liaison/ QA Officer _____ Phone _____

Type of Analysis:

Sample Type	Analysis For	Reporting Limit	Number of Samples
1			
2			
3			
4			

Methods Development: See attachment
Sample Storage: _____
Sample Storage: _____
Sample Extraction: _____
Analytical Standard Source: _____
Instrumentation: _____
Confirmation Method: _____
Continuing QC: See attachment
Sample Disposition: _____
Extract Disposition: _____
Reporting/Turnaround: See attachment
Cost of Analysis: See attachment

Other Specifications:

_____
_____
_____
_____
_____
_____
_____

Approved by: _____ _____ _____
CDPR Representative Lab Representative Date

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

METHODS DEVELOPMENT

Specifications		Validation*		
Method #	______			
Sample Matrix:	______	Sample Type	Spike Level	# Reps
Analyzed For:	______	1		
Reporting Limit:	______	2		
Other Specifications:	______	3		
______		4		
______		5		
______				
______				
Method #	______			
Sample Matrix:	______	Sample Type	Spike Level	# Reps
Analyzed For:	______	1		
Reporting Limit:	______	2		
Other Specifications:	______	3		
______		4		
______		5		
______				
______				
Method #	______			
Sample Matrix:	______	Sample Type	Spike Level	# Reps
Analyzed For:	______	1		
Reporting Limit:	______	2		
Other Specifications:	______	3		
______		4		
______		5		
______				

* Each laboratory shall determine a method detection limit (MDL), instrument detection limit (IDL), and a reporting limit (RL) for each analyte. Each laboratory shall also document their terms, definitions, and procedures for determining MDL, IDL, and RL in their approved analytical method. Each laboratory shall provide a copy of their approved analytical method before analyzing any field samples. The results from the method validation study will be used to establish recovery control limits for the field study.

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

CONTINUING QUALITY CONTROL

Reagent or Solvent Blanks
Reagent or Solvent Spikes
Blank-Matrix Spikes
Matrix Spike Level
Matrix Spike Level
Matrix Spike Level
Matrix Spike Level
Actual Matrix Spikes
Replicate Matrix Analyses

Replicate Extract Injections

Confirmation Analyses

For Well Samples:

Primary Samples
Backup Samples
Field Blank Samples

Storage Dissipation Study

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

REPORTING PROCEDURES

Completing the Chain of Custody Record:

1. Sign and date the box marked "Received for Lab by:".
2. Write in the Lab I.D. number in the appropriate space.
3. Results should be reported as follows:

4. For those samples which contain no detectable amount write "none detected" and indicate the reporting limit.
5. The chemist who analyzed the sample should sign and date in the appropriate space.
6. Write in the date of extraction and analysis in the appropriate space.

See attached Chain of Custody for an example.

Turnaround Time:

Additional Specifications:

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

BUDGET

Contract #: _____

Analysis	Number of Analyses	Cost per Analysis	cost

Total Cost = _____

Please send all reports and invoices to:

Attn:
California Department of Pesticide Regulation
1020 N Street, Rm. # 161
Sacramento, California 95814-5604

APPENDIX 1

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a signifi-

cantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right]$$

$$S = (S^2)^{1/2}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha\,=\,0.99)}\ (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha\,=\,.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ 1-\alpha\,=\,.99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which

affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

Project No. _____ Lab _____
Lab Project Manager _____ Phone _____
Project Chemist _____ Phone _____
EHAP Project Manager _____ Phone _____
EHAP Lab Liaison/ QA Officer _____ Phone _____

Type of Analysis:

	Sample Type	Analysis For	Reporting Limit	Number of Samples
1				
2				
3				
4				

Methods Development: See attachment
Sample Storage: _____
Sample Storage: _____
Sample Extraction: _____
Analytical Standard Source: _____
Instrumentation: _____
Confirmation Method: _____
Continuing QC: See attachment
Sample Disposition: _____
Extract Disposition: _____
Reporting/Turnaround: See attachment
Cost of Analysis: See attachment

Other Specifications:

_____
_____
_____
_____
_____
_____
_____

Approved by: _____ _____ _____
CDPR Representative Lab Representative Date

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

METHODS DEVELOPMENT

Specifications			Validation*	
Method # ____________				
Sample Matrix: ____________		Sample Type	Spike Level	# Reps
Analyzed For: ____________	1			
Reporting Limit: ____________	2			
Other Specifications: ____________	3			
____________	4			
____________	5			
____________				
____________				

Specifications			Validation*	
Method # ____________				
Sample Matrix: ____________		Sample Type	Spike Level	# Reps
Analyzed For: ____________	1			
Reporting Limit: ____________	2			
Other Specifications: ____________	3			
____________	4			
____________	5			
____________				
____________				

Specifications			Validation*	
Method # ____________				
Sample Matrix: ____________		Sample Type	Spike Level	# Reps
Analyzed For: ____________	1			
Reporting Limit: ____________	2			
Other Specifications: ____________	3			
____________	4			
____________	5			
____________				

* Each laboratory shall determine a method detection limit (MDL), instrument detection limit (IDL), and a reporting limit (RL) for each analyte. Each laboratory shall also document their terms, definitions, and procedures for determining MDL, IDL, and RL in their approved analytical method. Each laboratory shall provide a copy of their approved analytical method before analyzing any field samples. The results from the method validation study will be used to establish recovery control limits for the field study.

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

CONTINUING QUALITY CONTROL

Reagent or Solvent Blanks
Reagent or Solvent Spikes
Blank-Matrix Spikes
Matrix Spike Level
Matrix Spike Level
Matrix Spike Level
Matrix Spike Level
Actual Matrix Spikes
Replicate Matrix Analyses

Replicate Extract Injections

Confirmation Analyses

For Well Samples:

Primary Samples
Backup Samples
Field Blank Samples

Storage Dissipation Study

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

REPORTING PROCEDURES

Completing the Chain of Custody Record:

1. Sign and date the box marked "Received for Lab by:".
2. Write in the Lab I.D. number in the appropriate space.
3. Results should be reported as follows:

4. For those samples which contain no detectable amount write "none detected" and indicate the reporting limit.
5. The chemist who analyzed the sample should sign and date in the appropriate space.
6. Write in the date of extraction and analysis in the appropriate space.

See attached Chain of Custody for an example.

Turnaround Time:

Additional Specifications:

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

BUDGET

Contract #: _____

Analysis	Number of Analyses	Cost per Analysis	cost

Total Cost = _____

Please send all reports and invoices to:

Attn:
California Department of Pesticide Regulation
1020 N Street, Rm. # 161
Sacramento, California 95814-5604

SUPPLEMENT 7

Chemistry Laboratory Method Validation Results

CALIFORNIA DEPT. OF FOOD & AGRICULTURE
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, CA. 95832
(916) 262-2080 Fax (916) 262-1572

Method # : 62.5
Revised:
Original Date: 4/16/1998

Determination of Atrazine, Simazine, Diuron, Prometon, Bromacil, Prometryn, Hexazinone, Cyanazine, Metribuzin in River Water

Scope: This method is for the determination of atrazine, simazine, diuron, prometon, bromacil, prometryn, hexazinone, cyanazine, metribuzin in river water. The reporting limits for this method are: 0.05 ppb for atrazine, simazine, diuron, prometon, bromacil, prometryn, and 0.2 ppb for hexazinone, cyanazine, metribuzin.

Principal: Atrazine, simazine, diuron, prometon, bromacil, prometryn, hexazinone, cyanazine, metribuzin in river water are extracted with methylene chloride. The extract is evaporated to almost dryness, exchanged to methanol and passed through a conditioned C18 sep-pak for HPLC-UV and GC-NPD analyses.

Reagents and Equipments:

Reagents:

1. Solvents: Acetonitrile, methanol, water (HPLC Grade)
   Methylene chloride (Pesticide quality or equivalent)
2. Sodium sulfate- (ACS) Granular, anhydrous
3. Individual stock standard solutions (1 mg/mL): Obtain standards from Standards Repository, California Department of Food and Agriculture, Center for Analytical Chemistry, 3292 Meadowview Rd. Sacramento, CA 95832

Equipments:

1. Rotary Evaporator
2. Nitrogen evaporator, Organomation Model # 112
3. Boiling flask - 500-mL, with standard taper to fit rotary evaporator
4. Separatory funnel - 1000-mL, with TFE stopcock
5. Graduated test tube - 15-mL
6. Syringe - 10-mL
7. Graduated cylinders - 1000-mL, 250-mL
8. Acrodisc®, 0.2 µm filter. Gelman Sciences
9. Balance - Analytical
10. C18 sep-pak

Analysis:

Sample Extraction:

1. Remove sample from the refrigerator and bring it to room temperature.
2. Mix the sample well, weigh 500.0 g of the sample and transfer into a 1000-mL separatory funnel.

Analysis:

Sample Extraction:(cont.)

3. Add 75 mL of methylene chloride to the separatory and gently shake for two minutes *with periodic venting to release excess pressure*. Allow the organic layer to separate from water layer. If the emulsion interface between layers occurs, the analyst must employ a mechanical technique such as stirring using a glass rod to complete the phase separation. Drain the bottom organic layer through a 75-cm funnel which contains glasswool and 40 g of sodium sulfate into a 500-mL boiling flask.
4. Repeat step # 3 two more times.
5. Evaporate the extract to just about dryness using a rotary evaporator set at 40 °C, and a vacuum of 20 inches Hg.
6. Transfer the residue from the flask into a 15-mL graduated test tube using 10 mL of methanol.
7. Condition a C18 sep-pak with 5 mL of methanol, pass the 10 mL extract through the conditioned C18 sep-pak connected with a 0.2 um HPLC filter into a 15-mL graduated test tube.
8. Concentrate the extract from 10 mL to 1 mL using a Nitrogen evaporator set at 40 °C.
9. Mix well and transfer the extract into two microvials. One is for HPLC- UV analysis and the other for GC-NPD analysis.

Instrument Condition:

HPLC-UV Parameter for atrazine, simazine, bromacil, diuron:

Instrument: HPLC HP-1050 with a UV Variable Wavelength Detector.
Detector: UV Variable Wavelength.
Wavelength: 280 nm.
Time table:

	Wavelength
6.20 min.	238 nm
13.80 min.	280 nm

Column: Ultrasphere ODS 5 µm 4.6 mm x 25 cm.
Guard column: Ultrasphere ODS 5 µm 4.6 mm x 5 cm.
Mobile phase: Isocratic 40% ACN, 60% Water.
Flow rate: 1 mL per minute.
Injected volume: 20 µL.
Retention time:

Bromacil:	5.80 min.
Simazine:	6.60 min.
Atrazine:	10.30 min.
Diuron :	11.20 min.

Stop time: 20 min.

HPLC-UV Parameter for hexazinone, cyanazine, metribuzin:

Instrument: HPLC HP-1050.
Detector: UV Variable Wavelength.
Wavelength: 238 nm.
Column: Ultrasphere ODS 5 µm 4.6 mm x 25 cm.
Guard column: Ultrasphere ODS 5 µm 4.6 mm x 5 cm.

Analysis:

Instrument Condition:

HPLC-UV Parameter for hexazinone, cyanazine, metribuzin:(cont.)

Mobile phase: Isocratic 30% ACN, 70% Water.

Flow rate: 1 mL per min.

Injected volume: 20 µL.

Retention time: Hexazinone: 8.68 min.
Cyanazine: 12.21 min.
Metribuzin: 13.54 min.

Stop time: 20 min.

GC-NPD parameter for atrazine, simazine, prometon, prometryn:

Instrument: GC HP- 6890.

Column: HP-35 35% Phenyl Methyl Siloxane 30 m x 0.53 mm x 1.0 um

Oven temperature: Initial temp: 70 °C
Initial time : 1.00 min
Ramps: 10 °C per min.
Final temp: 280 °C
Final time: 5 min.
Run time: 27 min.

Detector: NP Detector
Temperature: 300 °C
Hydrogen flow: 3.0 mL/min.
Air flow: 60.0 mL/min.
Mode: Constant column + make up (helium) = 30.0 mL/min.
Adjust offset: 50.00

Injector: Splitless
Temperature: 250 °C
Pressure: 4.1 psi
Injected volume: 3 µL.

Retention time: Prometon: 15.87 min.
Atrazine: 16.21 min.
Simazine: 16.31 min.
Prometryn: 17.76 min.

Calculations:

The results to be reported in part per billion (ppb) :

$$\textbf{ppb (ng/g)} = \frac{\text{ng/µL (from standard curve) x final volume (µL)}}{\text{Sample weight (g)}}$$

Method performance:

Quality Control:

1. Sample storage: All field samples shall be kept refrigerated at 4 °C until extracted.
2. Sample extraction: All extracts shall be kept frozen at -10 °C until analyzed.
3. Freezer, refrigerator and oven temperatures shall be monitored and recorded daily.

Method performance:

Quality Control:(cont.)

4. A 3-point or more calibration curve shall be obtained at the beginning and the end of each set of samples.
5. For each set of samples, one matrix blank, one distilled water blank, and one matrix spike shall be included, and each set of samples shall not contain more than twelve samples. Each sample shall be injected two times to determine reproducibility of the analysis.

Recovery data:

The analytical method was validated by preparing five sets of sample. Each set contained four different levels of spike, a distilled water blank, and a matrix blank. Each set was processed through the entire analytical method at a different time and the following results were tabulated:

For Atrazine:

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.100	0.099	99.0
0.100	0.098	98.0
0.100	0.103	103
0.100	0.096	96.0
0.100	0.096	96.0
0.500	0.400	80.0
0.500	0.458	91.6
0.500	0.472	94.4
0.500	0.504	101
0.500	0.476	95.2
2.000	2.168	108
2.000	1.860	93.0
2.000	2.133	107
2.000	1.890	94.5
2.000	1.975	98.8
6.000	6.340	106
6.000	6.420	107
6.000	6.440	107
6.000	6.400	107
6.000	6.474	108.

For Simazine:

0.100	0.108	108
0.100	0.098	98.0
0.100	0.099	99.0
0.100	0.099	99.0
0.100	0.125	125
0.500	0.447	89.4
0.500	0.468	93.6
0.500	0.503	101
0.500	0.529	106

Method performance:

Recovery data:

For Simazine:(cont.)

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.500	0.487	97.4
2.000	1.881	94.1
2.000	1.845	92.3
2.000	2.126	106
2.000	2.063	103
2.000	2.027	101
6.000	6.294	105
6.000	6.000	100
6.000	6.440	111
6.000	6.400	107
6.000	6.372	106

For Diuron:

0.100	0.090	90.0
0.100	0.102	102
0.100	0.102	102
0.100	0.071	71.0
0.100	0.082	82.0
0.500	0.418	83.6
0.500	0.422	84.4
0.500	0.451	90.2
0.500	0.466	93.2
0.500	0.479	95.8
2.000	1.694	84.7
2.000	1.731	86.6
2.000	2.042	102
2.000	1.689	84.5
2.000	1.910	95.5
6.000	5.714	95.2
6.000	5.420	90.3
6.000	6.230	104
6.000	5.618	93.6
6.000	5.934	98.9

For Prometon:

0.100	0.096	96.0
0.100	0.085	85.0
0.100	0.089	89.0
0.100	0.095	95.0
0.100	0.083	83.0
0.500	0.464	92.8
0.500	0.415	83.0
0.500	0.464	92.8

Method performance:

Recovery data:

For Prometon:(cont.)

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.500	0.428	85.6
0.500	0.409	81.8
2.000	1.950	97.5
2.000	1.820	91.0
2.000	2.157	108
2.000	1.765	88.3
2.000	1.684	84.2
6.000	5.604	93.4
6.000	4.956	82.6
6.000	5.894	98.2
6.000	5.110	85.2
6.000	4.958	82.6

For Prometryn:

0.100	0.104	104
0.100	0.091	91.0
0.100	0.099	99.0
0.100	0.086	86.0
0.100	0.086	86.0
0.500	0.492	98.4
0.500	0.441	88.2
0.500	0.511	102
0.500	0.436	87.2
0.500	0.433	86.6
2.000	1.992	99.6
2.000	1.921	96.1
2.000	2.119	106
2.000	1.807	90.4
2.000	1.665	83.3
6.000	6.000	100
6.000	5.336	88.9
6.000	6.190	103
6.000	5.350	89.2
6.000	5.228	87.1

For Bromacil:

0.100	0.099	99.0
0.100	0.098	98.0
0.100	0.087	87.0
0.100	0.094	94.0
0.100	0.089	89.0
0.500	0.458	91.6
0.500	0.475	95.0

Method performance:

Recovery data:

For Bromacil:(cont.)

Spiked levels (ng/g)	Results (ng/g)	Recovery (%)
0.500	0.506	101
0.500	0.466	93.2
0.500	0.498	99.6
2.000	1.861	93.1
2.000	1.867	93.4
2.000	2.079	104
2.000	1.991	99.6
2.000	2.142	107
6.000	6.086	101
6.000	5.852	97.5
6.000	6.408	107
6.000	6.212	104
6.000	5.972	99.5

For Hexazinone:

0.300	0.298	99.3
0.300	0.299	99.7
0.300	0.298	99.3
0.300	0.307	102
0.300	0.365	122
0.500	0.428	85.6
0.500	0.453	90.6
0.500	0.524	105
0.500	0.444	88.8
0.500	0.534	107
2.000	1.927	96.4
2.000	1.951	97.6
2.000	2.009	101
2.000	2.066	103
2.000	2.100	105
6.000	5.984	99.7
6.000	5.530	92.2
6.000	5.980	99.7
6.000	5.900	98.3
6.000	6.244	104

For Cyanazine:

0.300	0.330	110
0.300	0.293	97.8
0.300	0.279	93.0
0.300	0.295	98.3
0.300	0.295	98.3
0.500	0.445	89.0

Method performance:

Recovery data:

For Cyanazine:(cont.)

0.500	0.475	95.0
0.500	0.455	91.0
0.500	0.467	93.4
0.500	0.465	93.0
2.000	2.191	110
2.000	2.137	107
2.000	2.058	103
2.000	2.115	106
2.000	2.063	103
6.000	6.080	101
6.000	6.282	105
6.000	6.526	109
6.000	6.348	106
6.000	6.310	105

For Metribuzin:

0.300	0.296	98.7
0.300	0.289	96.3
0.300	0.287	95.7
0.300	0.259	86.3
0.300	0.271	90.3
0.500	0.434	86.8
0.500	0.458	91.6
0.500	0.462	92.4
0.500	0.438	87.6
0.500	0.452	90.4
2.000	1.863	93.2
2.000	1.859	93.0
2.000	1.827	91.4
2.000	1.937	96.9
2.000	1.777	88.9
6.000	5.400	90.0
6.000	5.862	97.7
6.000	5.836	97.3
6.000	5.358	89.3
6.000	5.984	99.7

Method detection limit:

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably. To determine the MDL, 7 replicated background samples were spiked at 0.050 µg (for atrazine, simazine, diuron, prometon, prometryn), and 0.200 µg (for hexazinone, cyanazine, metribuzin). The standard deviations derived from the spiked samples were used to calculate the MDL using the following equation:

Method performance:

Method detection limit:(cont.)

$$MDL = t\,S$$

where:

t is the Student t value for the 99% confidence level with n-1 degrees of freedom (n-1, 1 - α = 0.99) which is 3.143, n represents the number of replicates which is 7.

S denotes the standard deviation obtained from replicate analyses.

The MDL and RL were tabulated as follow:

Chemical	Method detection limit (ppb)	*Reporting limit (ppb)
Atrazine	0.026	0.050
Simazine	0.014	0.050
Diuron	0.031	0.050
Prometon	0.026	0.050
Bromacil	0.025	0.050
Prometryn	0.023	0.050
Hexazinone	0.048	0.200
Cyanazine	0.040	0.200
Metribuzin	0.062	0.200

*Reporting limit (RL) refers to the level which quantitative results may be obtained usually 1-5 times the MDL

Dicussion:

Standards for quantitation of prometon, atrazine, simazine, and prometryn by GC/NPD must be made from the matrix blank extracts to compensate for the matrix enhanced response.

Confirmations:

All positve samples at reporting limits or above will be confirmed by APCI-LC/MS/MS.

WRITTEN BY: Duc Tran

TITLE: Agricultural Chemist II

APPROVED BY: Catherine Cooper

TITLE: Agricultural Chemist III

Appendix I: *Recovery data for determination of method detection limits*

For Atrazine:

Spiked level (μg)	Results (μg)	Recovery (%)
0.050	0.048	96.0
0.050	0.046	92.0
0.050	0.047	94.0
0.050	0.056	112
0.050	0.046	92.0
0.050	0.042	84.0
0.050	0.048	96.0

For Simazine:

0.050	0.051	102
0.050	0.053	106
0.050	0.049	98.0
0.050	0.056	112
0.050	0.052	104
0.050	0.051	102
0.050	0.051	102

For Diuron:

0.050	0.045	90.0
0.050	0.045	90.0
0.050	0.046	92.0
0.050	0.055	110
0.050	0.053	106
0.050	0.041	82.0
0.050	0.047	94.0

For Bromacil:

0.050	0.040	80.0
0.050	0.044	88.0
0.050	0.040	80.0
0.050	0.048	96.0
0.050	0.042	84.0
0.050	0.039	78.0
0.050	0.049	98.0

For Prometon:

0.050	0.045	90.0
0.050	0.050	100
0.050	0.050	100
0.050	0.058	116
0.050	0.048	96.0
0.050	0.049	98.0
0.050	0.053	106

Appendix I: *Recovery data for determination of method detection limits (cont.)*

For Prometryn:

Spiked level (µg)	Results (µg)	Recovery (%)
0.050	0.047	94.0
0.050	0.042	84.0
0.050	0.039	78.0
0.050	0.048	96.0
0.050	0.038	76.0
0.050	0.042	84.0
0.050	0.042	84.0

For Hexazinone:

0.200	0.187	93.5
0.200	0.196	98.0
0.200	0.191	95.5
0.200	0.180	90.0
0.200	0.184	92.0
0.200	0.184	92.0
0.200	0.201	101

For Cyanazine:

0.200	0.219	110
0.200	0.216	108
0.200	0.227	114
0.200	0.228	114
0.200	0.220	110
0.200	0.215	108
0.200	0.231	116

For Metribuzin:

0.200	0.204	102
0.200	0.195	90.0
0.200	0.196	98.0
0.200	0.205	103
0.200	0.216	108
0.200	0.185	92.5
0.200	0.197	98.5

CALIFORNIA DEPT. OF FOOD & AGRICULTURE
CHEMISTRY LABORATORY SERVICES
ENVIRONMENTAL MONITORING SECTION
3292 Meadowview Road
Sacramento, CA 95832
(916) 262-2080
Fax (916) 262-2082

Original Date: March 1, 1992
Supersedes: none
Current Date: May 18, 1998
Method #:36.3

Dicamba, MCPA, 2,4-D, 2,4,5-T, Triclopyr and Bentazon in River Water by GC/MSD

Scope: This method is for the determination of Dicamba, MCPA 2,4-D, 2,4,5-T, Triclopyr and Bentazon in River water. The reporting limit of this method is 0.1 ppb for all compounds.

Principle: The water sample is acidified below pH 1. The protonated Dicamba, MCPA 2,4-D, 2,4,5-T, Triclopyr and Bentazon are extracted with 1:1 petroleum ether : diethyl ether. The residues are derivatized with diazomethane, and analyzed by gas chromatography on a capillary column using a mass selective detector (MSD).

Reagents and Equipment:

Reagents:

1. Petroleum ether, grade suitable for pesticide residue analysis.
2. Diethyl ether, grade suitable for pesticide residue analysis.
3. Sulfuric acid, concentrated, A.C.S. reagent grade.
4. Hydrochloric acid, concentrated, A.C.S. reagent grade.
5. Ethanol, 95%.
6. Potassium hydroxide, A.C.S reagent grade.
7. N-methyl-1-nitroso-p-toluenesulfonamide, Aldrich D2,800-0
8. Sodium sulfate, anhydrous, suitable for pesticide residue analysis.
9. Diazomethane (see below)
10. Citral, 95% mixture of cis and trans.

Equipment:

1. Rotary evaporator (Büchi/Brinkmann, R110).
2. Nitrogen evaporator (Organomation Model #12).
3. Distillation kit (Aldrich Z 10025-0)
4. Hotplate with magnetic stirrer, 10"x10"
5. Balance, Mettler PC 4400

PREPARATION OF DIAZOMETHANE:

Diazomethane is Explosive and Carcinogenic-use caution and protective measures (read MSDS)

Preparation of Diazomethane: continued

Diazomethane is prepared from N-methyl-1-nitroso-p-toluenesulfonamide. Assemble a (cat #Z10,025-0) distillation apparatus according to the Aldrich Technical Information Bulletin number AL-131.

The reaction flask is placed in a 65°C water bath on a hot plate with a magnetic stirring control. A 0.5-inch stirring bar is placed in the reaction flask and a 1-inch stirring bar is placed in the water bath. Both magnetic bars should be stirring. Place a separatory funnel in the side arm of the Claisen adapter. Add 10 mL of 95% ethanol to a solution of 5 g KOH in 8 mL water in the reaction flask. Five grams of N-methyl-1-nitroso-1-toluenesulfon amide crystals are carefully dissolved in 100 mL ether and transferred into the separatory funnel. The crystals are moderately soluble in ether. Carefully open the stopcock of the funnel to allow the solution to drain into the reaction flask at a slow rate of about 1 hour for the entire 100 mL solution. Add an additional 20 mL of ether to rinse the separatory funnel and drain it into the reaction flask. Diazomethane formed in the reaction is distilled, condensed and collected into a 500 mL flask in an ice bath. After completing the distillation, transfer the diazomethane solution to a 4 ounce brown bottle with a Teflon-lined cap and store it in the freezer. This solution should be good for about a month in the freezer.

Analysis:

Sample Preparation:

1. Wash all glassware with 1N HCl, rinse with deionized water and dry them in a 90°C oven.
2. Allow sample to equilibrate to ambient temperature. Measure 800 mL (or by weight) of the sample to be analyzed into a 1-liter separatory funnel and record the volume or the weight to one decimal point.
3. Add 2.5 mL of the concentrated sulfuric acid to the water slowly and mix well.
4. Add 150 mL of 1:1 petroleum ether : diethyl ether (v/v). Shake it vigorously for 1.5 minutes. ***Vent frequently as pressure builds rapidly.***
5. Allow the phases to separate. Drain the aqueous layer into a 1-liter beaker.
6. Pour the organic phase from the top of the separatory funnel into a 500-mL acid-washed beaker. Transfer the aqueous phase back to the separatory funnel.
7. Repeat steps 4 through 6 twice. Combine the extracts.
8 Add approximately 20 mL of anhydrous sodium sulfate to the solvent extracts and immediately stir with a Teflon rod to remove any water.
9. Pour the dried solvent to an acid-washed 500-mL boiling flask.
10. Rinse the beaker with 20 mL of the 1:1 ether mix and combine in the flask.
11. Evaporate the solvent to about 1-3 mL on a rotary evaporator at 35° C and 20 inches of vacuum.

Derivatization of the Residues:

1. Add 2 mL of the diazomethane solution to the residue in the flask.
2. Allow the reagent to contact the inside surface of the flask by swirling gently and let the reaction mixture sit in fume hood covered with aluminum foil for 20 minutes. (If the brownish-yellow color has disappeared within 20 minutes, add additional diazomethane and let the reaction mixture sit for another 20 minutes.

Derivatization of the Residues: continued

3. Evaporate the solvent and the excess reagent to just dryness at ambient temperature using a gentle stream of nitrogen.
4. Pipette 2 mL ethyl acetate into the flask and swirl. Make sure no significant solvent evaporation occurs before transferring the sample to an autosampler vial. Add 20 µL of 95 % Citral solution into the autosampler vial. The extract is ready for GC analysis.

Instrument Conditions:

Hewlett-Packard Model 6890 Gas Chromatograph equipped with a series 6890 Mass Selective Detector
Column: HP-5MS (5% Phenyl Methyl Siloxane), 30 m X 0.25 mm X 0.25 um film.
Carrier: Helium, 8.8 psi
Column oven temperature:

Initial temperature:	70°C hold for 1.0 minute
Program Rate	15°C/minute
Final	250°C hold for 4 minutes

Injector Temperature: 250°C

Transfer Line Temperature: 280°C

Ions Selected for SIM Acquisition:

Dicamba	188, 203, 234	start time: 6.0 min.
MCPA	141, 214, 216	start time: 9.1 min.
2,4-D	199, 234, 236	start time: 9.7 min.
Triclopyr	210, 212, 271	start time: 10.1 min.
2,4,5-T	209, 233, 268	start time: 10.6 min.
Bentazon	175, 212, 254	start time: 11.4 min.

Retention time:

Dicamba	8.7 min.
MCPA	9.1 min.
2,4-D	9.7 min.
Triclopyr	10.2 min.
2,4,5-T	10.8 min.
Bentazon	11.6 min.

Volume Injected: 2 microliter

Calculation:

$$\text{Analyte (ppb)} = \frac{PA1}{PA2} \times \frac{FV}{W} \times SC \times 1000$$

Where:

PA1 = peak area of analyte from injected sample volume
PA2 = peak area of analyte standard
FV = final volume of sample extract (in mL)
W = sample weight (in grams)
SC = standard concentration (in ng/mL)

Method Performance:

Method Detection Limit(MDL)

Method Detection Limit refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. This was determined by fortifying seven aliquots of background water with 0.2 ppb of Dicamba, MCPA, 2,4--D, Triclopyr, 2,4,5-T and Bentazon then processing through the entire method along with a blank. The standard deviation derived from the 7 spiked samples was used to calculate the MDL using the following equation:

$$MDL = t\,S$$

where:

t is the Student 't' value for the 99% confidence level with n-1 degrees of freedom (n-1, 1 - α = 0.99), which is 3.143. n represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses.

COMPOUND	S (standard deviation, ppb)	MDL (ppb)
Dicamba	0.020	0.064
MCPA	0.014	0.045
2,4-D	0.013	0.041
Triclopyr	0.014	0.044
2,4,5-T	0.0196	0.062
Bentazon	0.01	0.031

Reporting Limit(RL)

It refers to the level above which quantitative results may be obtained. In this method the reporting limit is 0.1 ppb for all six compounds.

Recovery Data

The analytical method was validated by preparing 5 sets of spike samples. Each set contained four levels of spikes (0.2, 0.5, 2 and 10 ppb) and a matrix blank. the matrix was background water supplied by Dept. of Pesticide Regulation. All samples were processed through the entire analytical method. Recoveries of these compounds are summarized in the table below.

Method Validation Recovery Data:

Chemical Name	Spike Levels (ppb)	Recovery (%)	$\bar{x}$ (ppb)	Standard Deviation (ppb)	n
Dicamba	0.2	85.8	0172	0.022	5
	0.5	94	0.47	0.012	5
	2.0	106	2.11	0.130	5
	10.0	112	11.18	0.634	5

Recovery Data: continued

Chemical Name	Spike Levels (ppb)	Recovery (%)	$\bar{x}$ (ppb)	Standard Deviation (ppb)	n
MCPA	0.2	104	0.207	0.014	5
	0.5	99.2	0.496	0.018	5
	2.0	105	2.106	0.187	5
	10.0	92.4	9.242	0.912	5
2,4-D	0.2	96.3	0.193	0.010	5
	0.5	90.6	0.453	0.035	5
	2.0	100	2.006	0.204	5
	10.0	82.3	8.234	0.932	5
Triclopyr	0.2	110	0.220	0.018	5
	0.5	111	0.554	0.033	5
	2.0	116	2.326	0.236	5
	10.0	95.6	9.560	0.911	5
2,4,5-T	0.2	99.2	0.198	0.004	5
	0.5	95.1	0.475	0.038	5
	2.0	103	2.05	0.099	5
	10.0	98.3	9.834	0.786	5
Bentazon	0.2	102	0.204	0.016	5
	0.5	94.0	0.470	0.055	5
	2.0	97	1.938	0.106	5
	10.0	95.1	9.512	0.972	5

Discussion:

Our experience indicated that with this method all glassware must be rinsed with acid to ensure a decent recovery.

The diethyl ether should be checked for any interfering peaks before using for extraction. If interfering peaks are present in the diethyl ether distillation is recommended.

Considerable peak sharpening was obtained by adding 20 µl of 95% Citral solution to ~1 mL standard and sample extracts before analysis.

References:

Lee, Paul, *MCPA, DICAMBA and 2,4-D in River Water by GC/MSD, 3-22-93,* Environmental Monitoring Method, California Department of food and Agriculture.

UP DATED BY: Jean Hsu

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TITLE: Agricultural Chemist II

WRITTEN BY: Paul Lee

Paul Lee

TITLE: Agricultural Chemist III

REVIEWED BY: Catherine Cooper

Catherine Cooper

TITLE: Agricultural Chemist III Supervisor

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Center for Analytical Chemistry
Environmental Monitoring Section
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Original Date:01/10/97
Supersedes:none
Current Date:01/10/97
Method #:33.5

Determination of Glyphosate (N-phosphonomethyl glycine) in Runoff Water

Scope: This method is for the determination of glyphosate in runoff water by using HPLC with post-column derivatization and fluorescence detection. The detection limit and reporting limit for glyphosate using this procedure are 1.755 and 2.0 µg/L respectively.

Principles: A 500 mL sample of runoff water is acidified, and concentrated on a Chelex 100 (iron form) resin column. The residues, along with iron, are eluted with 6 N HCl. The $Fe(Cl)_4^-$, is removed from the residues by passage through an AG 1 x 8 resin column, an anion exchanger. The eluent is evaporated to dryness on a rotary evaporator. The glyphosate residue is redissolved in water and analyzed using HPLC with a post column derivatization system.

Reagents, Equipment and Instrument:

Reagents: All reagents must be suitable for pesticide residue analysis. Although some specific name brands are listed, equivalent supplies can be used:

1. Glyphosate, CAS # 1071-83-6, 1.0 mg/mL in water, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture).
2. Chelex® 100 resin, sodium form or iron form, 100-200 mesh, BioRad Laboratories, 2000 Alfred Nobel Dr., Hercules, Ca 94547. Contact the BioRad Laboratories for the sodium form to iron form conversion procedure.
3. Anion exchanger, AG® 1-X8 resin, Cl form, 200-400 mesh, BioRad Laboratories, 2000 Alfred Nobel Dr., Hercules, Ca 94547.
4. Deionized water, (DI water)
5. Hydrochloric acid.
6. Mobile phase: 0.005 M KH_2PO_4, pH 2.0, Pickering # K200.
7. Column Regenerant: Pickering RG019.
8. Hypochlorite diluent: pH 11.6, Pickering GA116, or dissolve 1.36 g KH_2PO_4, 11.6 g NaCl and 0.4 g NaOH in 500 mL DI water and dilute to 1000 mL with DI water.
9. Sodium hypochlorite: 5.25 % solution, Clorox™, or equivalent.
10. Hypochlorite solution: add 120 µL of 5.25% sodium hypochlorite to 1 L of hypochlorite diluent.
11. O-phthalaldehyde diluent: Pickering GA104, pH 10.4, or dissolve 19.1 g of sodium borate ($Na_2B_4O_7 \cdot 10\ H_2O$) in 1.0 L of DI water and adjust pH to 10.4 with

Reagents:continued

1 N NaOH solution.

12. OPA reaction solution: dissolve 100 mg of o-phthalaldehyde in 10 mL methanol. Pour this methanol solution to 950 mL OPA diluent and mix well. Pour the solution into the reagent reservoir and add 2 g of Thiofluor directly into it. Mix well (alternate: 1 mL of 2-Mercaptoethanol can be substituted for 2 g of Thiofluor).
13. Thiofluor™, N,N-Dimethyl-2-mercaptoethylamine-Hydrochloride, Pickering Laboratories, part# 3700-2000.
14. 2-Mercaptoethanol.
15. O-phthalaldehyde, Pierce Chemical Company.
16. Ferric chloride.

Equipment: Some specific name brands of equipment are listed, however, in most cases, equivalent equipment and supplies from various venders may be used.

1. Beakers, 150 mL
2. Flasks, 250 mL, round, flat-bottom.
3. Columns, chromatographic, with removable stopcock of PTFE and replaceable glass tip, 11 mm ID x 300 mm length, and 22 mm ID x 300 mm length, with 300 mL reservoir.
4. Steam bath with a nitrogen stream manifold.
5. Vacuum rotary evaporator, Büchi-Brinkman, RE 111.
6. Analytical column: Cation exchanger, K^+ form, 4 x 150 mm, Pickering 1954150.
7. Tubing, stainless steel or PEEK, 0.010" ID or less after columns and 0.020" ID before columns.
8. Guard column: Pickering # 1953020.
9. Microfilter, 0.2 µm nylon Acrodisc®, Gelman.

Instrument:

1. HPLC: Perkin Elmer Series 4 with column oven.
2. Post column system: Pickering dual pumps with a reaction coil after each pump. The first reaction coil is temperature controlled.
3. Autosampler, Perkin Elmer ISS-100.
4. Fluorescence Detector: The Toshiba model # 1000 was used to generate the validation data. Any detector capable of excitation at 340 nm and detecting an emission $\geq$ 455 nm may be used.
5. Integrator: A HP 3396 series 2 integrator

Analysis:

Preparation of Chelex 100 Resin column:

1. Plug column (2.2 cm OD x 25 cm with 300 mL reservoir) with glass wool.
2. Transfer ~ 20 mL DI water into the column. Measure and transfer 11 g of Chelex 100 resin (Fe form) into the column. Rinse down any resin on the walls with DI water. Drain and discard the water.

Sample Concentration with Chelex 100 Resin:

1. Mix sample well and then pour 500 mL into a beaker and record the weight.
2. Acidify the water sample with 6 N HCl to a pH of 2.0-2.3.
3. Add the acidified sample onto the column and elute at a rate of ~ 8 mL per minute. (If column becomes plugged and will not drain the top surface of sediment can be stirred gently so as not to disturb the column.)
4. After the sample has eluted, rinse the column walls with 50 mL DI water. Next turn the stopcock wide open and rinse with 100 mL 0.1 N HCl.
5. Add 3 mL 6 N HCl carefully, so as not to disturb the column and elute at a rate of ~ 10 drops per minute. Discard the eluent. Add 4 more mL and discard.
6. Elute the glyphosate with 6 mL of 6 N HCl at a rate of ~ 10 drops per minute. Collect the eluent into a 150 mL beaker. Repeat the elution procedure two more times collecting all eluent.
7. Add an additional 5 mL 6 N HCl onto the column and collect the eluent into the previously collected fraction. Add 5 mL concentrated HCl to the eluent to ensure the eluted iron complex is in the negatively charged form.

Preparation of Anion exchange column:

1. Plug a column (1.1 cm ID x 30 cm) with glass wool and add ~ 5 mL of DI water.
2. Transfer 7 g of AG 1-X8 anion exchange resin into the column.
3. With the stopcock wide open rinse the column with about 20-50 mL DI water.
4. Rinse the column twice with ~ 30 mL of 6 N HCl.
5. With the stopcock wide open, rinse the column with ~ 10 mL of 6 N HCl shortly before applying the sample.

Sample clean-up with an anion exchange column: AG 1x8 Resin

1. Transfer the sample onto the anion exchange column and elute with stopcock wide open. Collect the eluent into a 250 mL flat bottom flask.
2. Rinse the sample container with ~ 6 mL 6 N HCl and apply to the column.
3. Rinse the sample container with an additional 6 mL 6 N HCl and apply to the column.
4. Collect the rinse eluents into the corresponding 250 mL flask.

Concentration of the sample:

1. Evaporate the sample just to dryness on a rotary vacuum evaporator in a 65 °C water bath with 28-29 inches of vacuum. **To avoid sudden bumping, immerse the flask approximately 2-3 cm into the water for the first 3-5 minutes of evaporation.**
2. Place the flask on a 90 °C steam bath under a gentle stream of N_2 for 2-3 minutes to dry completely, then remove from the steam bath.
3. After the flask has cooled to room temperature, rinse down the sides of the flask with 2-mL DI water. Filter extract through a 0.2 µm filter into a 2-mL auto sampler vial for analysis.

Instrument Conditions:

Instrument: Perkin Elmer Series 4 HPLC with column oven and a Pickering post column system

Detector: Fluorescence: Excition, 340 nm & Emission, 465 nm

Column: Pickering Potassium Cation Exchange 4 mm x 150 mm x 8 µm

Instrument Conditions:continued

Guard Column: Glyphosate guard column k^+ form 3 x 20 mm
Column Temperature: 55 °C
Mobile Phase:
Eluent A: 0.005 M KH_2PO_4, pH 2.0
Eluent B: Column regenerent, or RG019

Time (min.)	Eluent A %	Eluent B %
1.0	100	0.0
15	100	0.0
2	0.0	100
6	100	0.0

Flow Rate: 0.4 mL/min.
Injection volume: 10 µL

Post Column System: Pickering
Derivatization Reagents: Hypochlorite solution & OPA solution
Flow Rate: 0.3 mL/min
Reaction Temperature: 31 °C
Retention time: Glyphosate, 8.6 ± 0.2 minutes

Calculation:

$$\mu g/L \text{ glyphosate} = \frac{\text{peak area of sample x final volume (mL) x 1000 (g/L)}}{\text{response factor x sample weight (g)}}$$

Where: response factor = $\dfrac{\sum (\text{peak area}_n / \text{std concentration}_n \text{ ug/mL})}{n}$

n = number of standards

Method Performance:

Quality Control:

1. A 4 point calibration curve of 0.5, 1.0, 2.0, and 4.0 ng/µL glyphosate was obtained at the beginning and the end of each set of samples.
2. Each sample shall be injected two times to insure reliability of the analysis. If the signal of a sample is greater than that of the highest standard in the calibration curve, dilute the sample. Reinject the diluted sample together with standards twice more. A sample set is usually comprised of 8 samples, a blank and a spike.

Recovery Data:

The analytical method was validated using 4 sets of spike samples. Each set contained 3 levels of spikes and a matrix blank. The matrix background water was supplied by Dept. of Pesticide Regulation. All samples were processed through the entire analytical method.

Analyte	Spike Level (µg/L)	Results (µg/L)	Recovery (%)
Glyphosate	4.0	2.35	58.8
		2.96	74.0
		2.37	59.3
		2.72	68.0
	20	14.9	74.9
		14.4	72.0
		14.8	74.0
		16.2	81.0
	100	81.7	81.7
		70.1	70.1
		78.4	78.4
		74.1	74.1

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. To determine the MDL, 7 samples each containing 500 mL of background surface water were spiked with 4 ug glyphosate. The standand deviation derived from the 7 spikes was used to calculate the MDL using the following equation:

$$MDL = S\ t$$

where:

t is the student's "t" value for the 99% confidence level with n-1 degrees of freedom (n-1,1-α = 0.99). n represents the number of replicates
S denotes the standard deviation obtained from replicate analyses.

Method Detection Limit (MDL): continued

Spike Recoveries for MDL Determination

Spike	Recovery µg/L
1	5.29
2	4.97
3	5.86
4	5.37
5	4.59
6	5.83
7	6.20

The standard deviation ascertained for glyphosate is 0.558 µg/L
The MDL is 1.755 µg/L for glyphosate.

Reporting Limit (RL):

RL refers to the level above which quantitative results may be obtained. The MDL was used as a guide for determining the RL. The reporting limit for this method is 2.0 µg/L which is the value obtained for the MDL rounded to the nearest whole number.

Discussion:

AG 1-X8 resin was successfully regenerated in our study. This was acomplished by adding approximately 30 mL of DI water to the column to wash off the iron. If the column starts to change back to its orginial color regeneration is possible. Let the water drain ~ half way down and then add ~ 10 mL of 6 N HCl. The column should turn a light yellow color. Let this solution drain completely and then wash the column with ~ 30 mL of DI water. The column should be back to the orginal color. Continue with step 4 in *Preparation of Anion Exchange Column* and the column is ready to reuse. The chemist must be alert to any adverse effects after several times of reuse.

The HPLC column should be stored in regenerant solution when not in use to prolong the life of the column. The column may need to be treated with Restore occassionaly when peak shape starts to broaden. Treat the column with Restore for 60 minutes, then rinse with the mobile phase for 30 minutes and try the column again. If this does not work it may be necessary to replace the column.

Irreversible damage to the column may be caused by solvent passing through the analytical column or running the column at high flow rates.

References:

1. Lee, Paul, *Determination of Glyphosate (N-phosphonomethyl glycine) and AMPA (Aminomethyl phosphonic acid) in Well Water by HPLC, with Post-column Derivatization and Fluorescence Detection*, 10-30-95, Enviromental Monitoring Methods, California Department of Food and Agriculture.

References:continued

2. Cowell, J., et al., "*Validation of an Analytical Residue Method for Analysis of Glyphosate and Metabolite: An Interlaboratory Study*", J. Agric. Food Chem. 1986, 34, 955-960.

3. Jerry R. Steinmetz "*Analytical Method for Glyphosate and AMPA in Raw Agricultural Commodities, and Their Processed Fractions, Document #Res-008-90*", Environmental Science Department, Monsanto Company, 700 Chesterfield Parkway North, St. Louis, Missouri 63198. Fax Number: (314) 537-6134.

4. US Environmental Protection Agency, " *Determination of Glyphosate in Drinking Water by Direct-Aqueous-Injection HPLC, Post-Column Derivatization, and Fluorescence Detection*", EPA-500 Series Supplement I, July 1990.

5. Communication with *Donna Harding of BioRad Laboratories* during September 1995, Customer Technical Support, BioRad Laboratories.

6. Communication with *Tony Le and Mark Tracy of Pickering Laboratories* during September 1995, 1951 Colony Street, Suite S, Mountain View, California 94043.

7. Mark E Oppenhuizen and John E. Cowell "*Liquid Chromatographic Determination of Glyphosate and Aminomethylphosphonic Acid (AMPA) in Environmental Water: Collaborative Study*" J. Assoc. Off. Anal. Chem. 74, January/ February 1991 Issue.

8. Pickering Laboratories "*Post-Column LC Systems for Environmental Pesticide Analysis" B-CA5, 1993,* 1951 Colony Street, Suite S, Mountain View, California 94043.

Written By:

Jane White

Title: Agricultural Chemist II

Approved By:

Catherine Cooper

Title: Agricultural Chemist III

172 A

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

Project No.	172- Pesticides in Forest Surface Water -Yurok	Lab	CDFA
Lab Project Manager	Cathy Cooper	Phone	262-2080
Project Chemist	D. Tran, J. Hernandez, H. Feng, J. White, J. Hsu	Phone	262-2074
EHAP Project Manager	Pam Wofford	Phone	324-4297
EHAP Lab Liaison/ QA Officer	Carissa Ganapathy	Phone	322-3082

Type of Analysis:

	Sample Type	Analysis For	Reporting Limit	Number of Samples
1	Surface Water	Triclopyr/2,4-D	0.1 ug/L	
2	Surface Water	Atrazine	0.05 ug/L	
3				
4				
5				

Methods Development: completed
Sample Storage: All samples to be kept refrigerated until extracted.
Sample Extraction: All extracts to be kept frozen until analyzed.
Analytical Standard Source: Normal sources
Instrumentation:
Confirmation Method:
Continuing QC: See attachment
Sample Disposition: Return unused portion of sample to EHAP warehouse
Extract Disposition: Comply with GLP requirements
Reporting/Turnaround: See attachment
Cost of Analysis: See attachment

Other Specifications:

Use provided N.F. Americ. Riv.background water for all quality control analyses.
This study is to be conducted under GLP.

Approved by:

Carissa Ganapathy 7/8/99
CDPR Representative

Catherine Cooper 7/15/99
Lab Representative

Date

172LBPa172

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

METHODS DEVELOPMENT AND VALIDATION

Specifications | **Validation***

Method # complete for all compounds listed
Sample Matrix: _____
Analyzed For: _____
Reporting Limit: _____
Other Specifications: _____

	Sample Type	Spike Level	# Reps
1			
2			
3			
4			
5			

Method # _____
Sample Matrix: _____
Analyzed For: _____
Reporting Limit: _____
Other Specifications: _____

	Sample Type	Spike Level	# Reps
1			
2			
3			
4			
5			

Method # _____
Sample Matrix: _____
Analyzed For: _____
Reporting Limit: _____
Other Specifications: _____

	Sample Type	Spike Level	# Reps
1			
2			
3			
4			
5			

* Each laboratory shall determine a method detection limit (MDL), instrument detection limit (IDL) and a reporting limit (RL) for each analyte. Each laboratory shall also document their terms, definitions and procedures for determining MDL, IDL and RL in their approved analytical method. Each laboratory shall provide a copy of their approved analytical method before analyzing any field samples.
The results from the method validation study will be used to establish recovery control limits for the field study.

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

CONTINUING QUALITY CONTROL

Reagent or Solvent Blanks: 1 blank matrix per extraction set

Reagent or Solvent Spikes:

Blank-Matrix Spikes: 2 duplicate matrix spikes per extraction set

Matrix: North Fork Americ. River — Spike Level: 2 X R.L.

Matrix: — Spike Level:

Matrix: — Spike Level:

Matrix: — Spike Level:

Actual Matrix Spikes:

Replicate Matrix Analyses:

Replicate Extract Injections:

Confirmation Analyses:

Samples to be analyzed:

Primary Samples: all primary samples to be analyzed

Backup Samples:

Field Blank Samples:

Storage Dissipation Study: completed for these compounds

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

REPORTING PROCEDURES

Completing the Chain of Custody Record:

1. Sign and date the box marked "Received for Lab by:".
2. Write in the Lab I.D. number in the appropriate space.
3. Results should be reported as follows:

All water samples to be reported in ug/L.

4. For those samples which contain no detectable amount write "none detected" and indicate the reporting limit.
5. The chemist who analyzed the sample should sign and date in the appropriate space.
6. Write in the date of extraction and analysis in the appropriate space.

See attached Chain of Custody for an example.

Turnaround Time: All samples to be extracted within 7 business days of date of sampling unless Lab Liaison is contacted

Cathy added: This may be later depending on number of days between sampling date and delivering to the lab
CA 7/16/99

Additional Specifications:

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
ANALYTICAL LABORATORY SPECIFICATIONS

BUDGET

Contract #: _____

Analysis	Number of Analyses	Cost per Analysis	Cost

Total Cost = _____

Please send all reports and invoices to:

California Department of Pesticide Regulation
3971 Commerce Drive, Suite D
West Sacramento, California 95691

Method Validation Data (% recoveries) for Phenoxy herbicides in surface water

Analyte	Spike Level ug/L	Recovery (%of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD	UCL	UWL	LWL	LCL
MCPA	0.1	81.0	91.0	85.0	96.0	78.0	86.2	7.33				
	0.5	96.0	97.8	96.6	101	104	99.1	3.36				
	2.0	104	106	115	91.0	112	106	9.29				
	10	107	82.5	91.9	87.8	93	92.4	9.122				
							95.8	10.23	126.5	116.3	75.4	65.1
2,4-D	0.1	96.0	95.0	96.0	71.0	116	94.8	15.96				
	0.5	83.4	85.0	95.8	89.0	99.6	90.6	6.96				
	2.0	97.0	98.0	114	87.0	105	100	10.03				
	10	96.1	70.1	80.9	80.5	84.1	82.3	9.324				
							92.0	12.17	128.5	116.3	67.6	55.5
Triclopyr	0.1	112	118	115	88.0	126	112	14.29				
	0.5	102	109	119	115	109	111	6.50				
	2.0	109	122	131	101	119	116	11.65				
	10	109	83.3	94.8	95.0	95.9	95.6	9.110				
							109	12.74	146.9	134.1	83.2	70.4

Method Validation Data (% recoveries) for Glyphosate in surface water

Analyte	Spike Level ug/L	Recovery (%of spike) Rep #1	Rep #2	Rep #3	Rep #4	Mean	SD	UCL	UWL	LWL	LCL
Glyphosate	4	58.8	74	59.3	68	65.0					
	20	74.9	72.0	74.0	81.0	75.5					
	100	81.7	70.1	78.4	74.1	76.1					
						72.2	7.33	94.2	86.9	57.5	50.2

Data from CDFA method 33.5
Chemist:J. White
Reporting Limit: 2.0 ug/L

Method Validation Data (% recoveries) for Triazines, Bromacil and Diuron in surface water

Analyte	Spike Level ug/L	Recovery (%of spike) Rep #1	Rep #2	Rep #3	Rep #4	Rep #5	Mean	SD	UCL	UWL	LWL	LCL
Atrazine	0.100	99.0	98.0	103	96.0	96.0	98.4	2.88				
	0.500	80.0	91.6	94.4	101	95.2	92.4	7.75				
	2.000	108	93.0	107	94.5	98.8	100.3	6.95				
	6.000	106	107	107	107	108	107.0	0.707				
							99.5	7.28	121.4	114.1	85.0	77.7
Simazine	0.100	108	98.0	99.0	99.0	125	105.8	11.48				
	0.500	89.4	93.6	101	106	97.4	97.5	6.43				
	2.000	94.1	92.3	106	103	101	99.3	5.86				
	6.000	105	100	111	107	106	105.8	3.96				
							102.1	7.87	125.7	117.8	86.4	78.5
Diuron	0.100	90.0	102	102	71.0	82.0	89.4	13.33				
	0.500	83.6	84.4	90.2	93.2	95.8	89.4	5.35				
	2.000	84.7	86.6	102	84.5	95.5	90.7	7.78				
	6.000	95.2	90.3	104	93.6	98.9	96.4	5.26				
							91.5	8.41	116.7	108.3	74.6	66.2
Prometon	0.100	96.0	85.0	89.0	95.0	83.0	89.6	5.81				
	0.500	92.8	83.0	92.8	85.6	81.8	87.2	5.29				
	2.000	97.5	91.0	108.0	88.3	84.2	93.8	9.29				
	6.000	93.4	82.6	98.2	85.2	82.6	88.4	7.05				
							89.8	6.94	110.6	103.6	75.9	68.9
Prometryn	0.100	104	91.0	99.0	86.0	86.0	93.2	8.04				
	0.500	98.4	88.2	102	87.2	86.6	92.5	7.18				
	2.000	99.6	96.1	106	90.4	83.3	95.1	8.68				
	6.000	100	88.9	103	89.2	87.1	93.6	7.30				
							93.6	7.25	115.3	108.1	79.1	71.9
Bromacil	0.100	99.0	98.0	87.0	94.0	89.0	93.4	5.32				
	0.500	91.6	95.0	101	93.2	99.6	96.1	4.07				
	2.000	93.1	93.4	104	99.6	107	99.4	6.22				
	6.000	101	97.5	107	104	99.5	102	3.75				
							97.7	5.59	114.5	108.9	86.5	80.9
Hexazinone	0.300	99.3	99.7	99.3	102	122	104.5	9.87				
	0.500	85.6	90.6	105	88.8	107	95.4	9.87				
	2.000	96.4	97.6	101	103	105	100.6	3.60				
	6.000	99.7	92.2	99.7	98.3	104	98.8	4.26				
							99.8	7.67	122.8	115.1	84.5	76.8
Cyanazine	0.300	110	97.8	93.0	98.3	98.3	99.5	6.29				
	0.500	89.0	95.0	91.0	93.4	93.0	92.3	2.32				
	2.000	110	107	103	106	103	105.8	2.95				
	6.000	101	105	109	106	105	105.2	2.86				
							100.7	6.65	120.6	114.0	87.4	80.7
Metribuzin	0.300	98.7	96.3	95.7	86.3	90.3	93.5	5.04				
	0.500	86.8	91.6	92.4	87.6	90.4	89.8	2.46				
	2.000	93.2	93.0	91.4	96.9	88.9	92.7	2.92				
	6.000	90.0	97.7	97.3	89.3	99.7	94.8	4.79				
							92.7	4.11	105.0	100.9	84.5	80.4

SUPPLEMENT 8

Generating Rinse Blanks

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE
Procedure for Generating Rinse Blanks

KEY WORDS-
Rinse; decontamination; splitter

APPROVALS

APPROVED BY: _____ DATE: 6/25/98
Management

APPROVED BY: Lisa Ross DATE: 6/24/98
EHAP Senior Scientist

APPROVED BY: Carissa Sumpathy DATE: 6/23/98
EHAP Quality Assurance Officer

PREPARED BY: Carissa Sumpathy DATE: 6/23/98

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Procedure for Generating Rinse Blanks

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1 .O INTRODUCTION

1 .1 Purpose

Rinse blanks are created to assess the efficacy of equipment decontamination procedures described in SOPs FSWA004 and FSWA005.

1.2 Scope

This document will provide specific instructions for collecting rinse blanks from surface water sampling equipment and/or the water splitting equipment.

2.0 MATERIALS

2.1 Deionized water (sufficient to fill sample bottles)
2.2 Sample bottles (same number used for surface water analysis)
2.3 Clean Geotech® Dekaport port splitter
2.4 All containers used to collect or contain samples: e.g. Teflon® bottle, Teflon® spout, stainless steel buckets, milkcan, funnels
2.5 Chain of Custody records
2.6 Latex disposible gloves
2.7 Level

3.0 PROCEDURES

Rinse Blanks should be performed at least once every study or after each sample that represents 10% of the total number of samples collected in the study, whichever is more. Enough rinse blanks should be generated to analyze all chemicals analyzed for in **a** particular study. Rinse blanks should be collected from both sampling and splitting equipment, or both combined if all the equipment is cleaned and split at one location. Below is an example describing the procedure used for generating rinse blanks when both sampling and splitting equipment are used at one location.

3.1 Instructions for Generating Rinse Blanks

3.1.1 After the samples have been collected at the sampling site and the equipment listed in 2.3 and 2.4 above have been completely decontaminated according to SOP#s FSWAO04 and FSWAO05, the rinse blank may be collected.

3.1.2 Place the cleaned Geotech® Dekaport water splitter on level ground. Make sure all splitter water spouts are level to ensure a fairly even water flow. Place a level across the top of the splitter to ensure that it is level.

3.1.3 While wearing disposable gloves, set up the same number of sample bottles as used for surface water analysis, following instructions for splitting procedures in FSWAO04.

3.1.4 Pour about 500ml more deionized water than required to fill the rinse blank sample bottles into the first piece of sampling equipment (e.g. Teflon@ bottle). Swirl the water around and then pour the water into the next piece of sampling equipment (e.g. the milkcan).

3.1.5 Continue to pour the water and swirl until the water has rinsed all the sampling equipment. Prior to completely pouring the remainder of the sample water out of the sampling containers swirl the water one last time to ensure that any residual sediment stays with the sample water and not at the bottom or along the sides of the container. Lastly, pour the deionized water through the Dekaport splitter and fill the rinse blank sample bottles. If there are extra splitter spouts, put a clean bucket under the spouts. Pour the water from this bucket back through the splitter. Continue the process until all the bottles are full.

3.1.6 Cap all bottles and prepare COCs in the same manner as surface water samples. Add the words "Rinse Blank" to the comments section of the Check-In Sheet. If samples need to be acidified, add three drops of 3N HCL. Store samples at 4°C.

3.1.7 Cover all containers and the splitter with clean plastic bags.

SUPPLEMENT 9

Archiving Study Data, Records, and Other Documents

California Department of Pesticide Regulation
Environmental Hazards Assessment Program
1020 N Street
Sacramento, California 95814

STANDARD OPERATING PROCEDURE
Archiving Study Data, Records, and Other Documents

KEY WORDS

archivist; quality assurance; SOP; project leader; check-in; check-out; GLP

APPROVALS

APPROVED BY: John S. Sanders DATE: 3/6/97
Management

APPROVED BY: [signature] DATE: 2-25-97
EHAP Senior Scientist

APPROVED BY: Randy Segawa DATE: 2-26-97
EHAP Quality Assurance Officer

PREPARED BY: [signature] DATE: 2-24-97

Environmental Hazards Assessment Program (EHAP) organization and personnel such as management, senior scientist, quality assurance officer, project leader, etc. are defined and discussed in SOP ADMN002.

STANDARD OPERATING PROCEDURE
Archiving Study Data, Records, and Other Documents

1.0 INTRODUCTION

1.1 Purpose

This Standard Operating Procedure (SOP) describes the archiving procedures for all records and data associated with studies conducted by the Environmental Hazards Assessment Program (EHAP), Department of Pesticide Regulation, California Environmental Protection Agency. This SOP should be followed for the archiving of all study data.

1.2 Definitions

Archivist is the individual responsible for maintaining the archives.

Project leader is the individual responsible for the overall conduct of a study.

Study file is the file containing all of the records and data for a study.

Study number is the unique identification number assigned to each study.

2.0 MATERIALS

none

3.0 PROCEDURES

3.1 Archived study files shall consist of all raw data, field notes, protocols, interim reports, and a master copy of the final report. Correspondence and other documents relating to interpretation and evaluation of data must also be included in the study file if they are not included in the final report. Raw data results will in most cases consist of the original chain of custody with the analytical result and chemist signature (white copy).

3.2 Study files will be retained by the project leader until the final report is approved. At that point, the project leader will give the study file to the archivist. During the period between initiation of the study and final report approval, the archivist will include the location of the study file in the archives index.

3.3 Archiving of study files must be done only by the archivist. The project leader must organize the study file so that information is readily retrievable from within the file.

3.4 The project leader shall provide the archivist with an electronic copy of the final report. For studies conducted under Good Laboratory Practices, additional requirements will apply (U.S. EPA, 1992), including the following:

3.4.1 Photocopied material shall not be included in the study file.

3.4.2 All field notes, data records, etc. must be in ink.

3.5 The archivist shall be the only individual with access to the archives. The archivist will designate an alternate when he/she is absent.

3.6 The study files shall be filed numerically by study number. The project leader must request a study number prior to the beginning of the study. Each protocol must have **a** study number for approval.

3.7 An index of the archived study files shall be kept by the archivist. Other individuals may have copies of this index upon request.

3.7.1 The index shall list the study files numerically by study number.

3.7.2 Each entry on the index shall list the study number, the date the study file was archived, and the title of the study.

3.7.3 The index shall list the location of files for studies still in progress, as stated in section 3.2

3.8 Requests for information contained in archived files will be made to the archivist. Check-in/out procedures are as follows:

3.8.1 Archivist retrieves study file.

3.8.2 The study file number is recorded on the check-in/out log. The check-out date will be recorded, and the archivist and requestor will initial it.

3.8.3 No alterations or additions shall be made to the files while in the borrower's

possession.

3.8.4 The study file shall be returned to the archivist by the same individual who checked it out. The file shall be returned in the same organized manner as it was checked out. The check-in date will be recorded in the log and the archivist and the borrower shall initial it.

3.8.5 The archivist is responsible for refiling the study file in the archives.

3.9 A check-in/check-out log will be kept by the archivist. This log shall contain the following information:

3.9.1 The study number.

3.9.2 The name of the borrower.

3.9.3 The check-out date.

3.9.4 The check-in date.

3.9.5 Spaces for the archivist and borrower to initial both the check-in and check-out dates.

3.10 Electronic copies of final reports will be stored indefinitely in a manner that prevents deterioration and insures that copies are easily accessible by the archivist. It is the responsibility of the archivist to manage these files, updating electronic format when appropriate. When updates are necessary, the archivist will state the type of change on the archive index, initial, and date the entry.

3.11 Study files will be retained for a minimum of five years. After that time, the archivist may continue storage of files, or transfer to another location. In all cases, study file transfers or disposals will be noted in the archives index.

4.0 REFERENCES

U.S. Environmental Protection Agency. 1989. Federal Insecticide Fungicide, and Rodenticide Act (FIFRA); Good Laboratory Practice Standards; Final Rule.

U.S. Environmental Protection Agency. 1992. Federal Insecticide Fungicide, and Rodenticide Act (FIFRA) Good Laboratory Practice Standards (GLPS) Questions and Answers. Office of Prevention, Pesticides, and Toxic Substances.